Benzylation of Nitroalkanes Using Copper-Catalyzed Thermal Redox Catalysis: Toward the Facile *C*-Alkylation of Nitroalkanes

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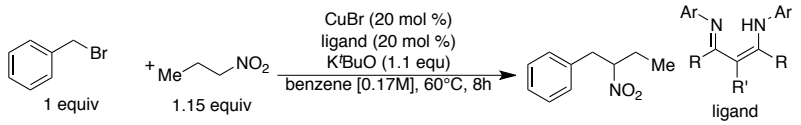
1. General Experimental Details. Toluene and dioxane were dried on alumina according to published procedures.[1] Hexanes and benzene were purchased in an anhydrous septa sealed bottle. Copper bromide and sodium *tert*-butoxide were purchased commercially; the bulk was stored in a nitrogen filled glovebox; samples were removed from the glovebox and stored in a desiccator under air for up to one week prior to use. All hot glassware was oven dried for a minimum of two hours or flame-dried under vacuum prior to use. β-Diketiminate ligand **4** was synthesized according to a published procedure.[2] Substrates 8-(bromomethyl)-quinoline[3], 2-(bromomethyl)thiophene[4], 2-bromomethyl-benzooxazole[5], 2-methyl-1-nitropropane[6], and 4-nitro-1-butene[7], methyl-4-nitrobutyrate[8], N,N-dimethyl-4-nitro-butanamide[9], 4-nitrobutyl acetate[10], nitrocyclohexane[11], and methyl 4-nitropentanoate[12] were prepared according to the literature procedure. All other substrates and reagents were purchased in highest analytical purity from commercial suppliers and used as received. Ligand optimization reactions reported in Table 2 were carried out in a glovebox (N_2 atmosphere) on a 500 μmol scale in 16 mm X 100 mm threaded test tubes sealed with Teflon lined caps and were heated in an aluminum block-heater with stirring. Product yields in Table 2 obtained by NMR unless otherwise noted. Product yields in Table S1 obtained by GC with dodecane as an internal standard. All other reactions, except that producing nitroalkane **38**, were set up using Schlenk technique and heated with stirring in temperature controlled oil baths. "Double manifold" refers to a standard Schlenk-line gas manifold equipped with nitrogen and vacuum (ca. 100 mtorr).

2. Instrumentation and Chromatography. 400 MHz ^{1}H, 101 MHz ^{13}C, and 376 MHz ^{19}F spectra were obtained on a 400 MHz FT-NMR spectrometer equipped with a Bruker CryoPlatform. 600 MHz ^{1}H and 151 MHz ^{13}C spectra were obtained on a 600 MHz FT-NMR spectrometer equipped with a Bruker SMART probe. ^{13}C spectra were recorded using Attached Proton Test phase pulse sequence; carbons with an odd number of protons are phased down and those with an even number of protons are phased up.[13] All samples were analyzed in the indicated deutero-solvent and were recorded at ambient temperatures. Chemical shifts are reported in ppm. ^{1}H NMR spectra were calibrated using the residual protio-signal in deutero-solvents as a standard. ^{13}C NMR spectra were calibrated using the deutero-solvent as a standard. IR spectra were recorded on an FT-IR spectrometer as thin films. Unless otherwise noted, column chromatography was performed with 40-63 μm silica gel with the eluent reported in parentheses. In specially marked reactions 5-20 μm silica gel was used to improve separation. Analytical thin-layer chromatography (TLC) was performed on precoated glass plates and visualized by UV or by staining with $KMnO_4$. GC samples were run on a Shimadzu GC 2010 Plus using a Thermo Scientific TR-1 column (10m X 0.1mm, ID 0.1μm film). All reported GC yields are corrected using dodecane as an internal standard. All NMR yields are reported using 1,3,5-trimethoxybenzene or hexamethylbenzene as an internal standard. GCMS data was collected using an Agilent 6850 series GC and 5973 MS detector. Low resolution ESI data was collected on a Thermo LCQ Advantage running in positive ion mode. High resolution mass spectrometry data was obtained at the University of Illinois at Urbana-Champaign.

Yields reported in tables of main text reflect the average isolated yields of at least two independent runs; any deviation between these yields and those reported in this supporting information reflect the difference between individual and average yields.

3. Additional Optimization of β-Diketiminate Ligands. Outlined in Table S1 is the series of experiments aimed at the optimization of the β-diketiminate ligand in the copper catalyzed nitroalkane benzylation reaction. Although a range of substituents were explored on both the nitrogen-aryl substituents, as well as the 1,3-diketone backbone, none of these derivatives proved more successful than the 2,6-dimethyl aniline derived ligand **4**. Due to its ease of synthesis and low cost, ligand **4** was selected as the ligand for further optimization (see main text). Synthesis of ligands **4**, **S1**, and **S4-S19** were carried out via the condensation of the appropriate 1,3 diketones and the corresponding aniline using a Dean-Stark condensor as described in the literature[2]. All reactions were run under air with the exception of **S10**, which was run under N_2. Ligands **S2**[14] and **S3**[15] were prepared by modification of published procedures.

Table S1. Ligand Optimization.



Entry	Ligand	R	R'	Ar	yield (%)[a]
1	**4**	Me	H	2,6-Me-C_6H_3	77
2	**S1**[b,c]	Et	H	2,6-Me-C_6H_3	76
3	**S2**[b,c]	^{i}Pr	H	2,6-Me-C_6H_3	80
4	**S3**[b,d]	^{t}Bu	H	2,6-Me-C_6H_3	40
5	**S4**[b,e]	Ph	H	2,6-Me-C_6H_3	4
6	**S5**[b,e]	Me	H	2-OMe-C_6H_4	44
7	**S6**	Me	H	2,6-^{i}Pr-C_6H_3	44
8	**S7**[b]	Me	Me	2,6-Me-C_6H_3	69
9	**S8**[b,f]	Me	H	2,6-Et-C_6H_3	78
10	**S9**[b]	Me	H	2,6-Me, 4-OMe-C_6H_2	79
11	**S10**	Me	H	2,4,6-Me-C_6H_2	80
12	**S11**	Me	H	2-CF_3-C_6H_4	37
13	**S12**[b]	Me	H	2-OCF_3-C_6H_4	64
14	**S13**	Me	H	2-Me, 4-OMe-C_6H_3	64
15	**S14**	Me	H	2,4,6-OMe-C_6H_2	47
16	**S15**[b,e]	Me	H	2-Me-C_6H_4	55
17	**S16**	Me	H	C_6H_5	28
18	**S17**	Me	H	4-OMe-C_6H_4	33
19	**S18**	Me	H	4-CF_3-C_6H_4	18
20	**S19**	Me	H	3,5-CF_3-C_6H_3	17

[a] All yields determined by GC with internal standard. [b] Toluene [0.17M] used as solvent. [c]Reaction time 28 h. [d]Reaction time 17 h. [e]Reaction time 12 h. [f]Reaction time 20 h.

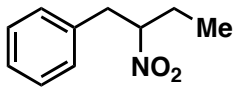
4. General Protocols for Nitroalkylation.

General Protocol A. Synthesis of Nitroalkanes with Liquid Benzyl Bromide Substrates: A hot 25 mL Schlenk flask equipped with magnetic stir bar and rubber septum was attached to a double manifold and cooled under vacuum. The flask was backfilled with N_2, the septum was removed, and CuBr (0.2 equiv), ligand **4** (0.25 equiv), and base (1.2 equiv) were added. The septum was replaced, the flask was attached to a double manifold, and evacuated and backfilled with nitrogen five times. Anhydrous solvent (6 mL), the nitroalkane (1.25 equiv), and the benzyl bromide (1.0 equiv) were added to the

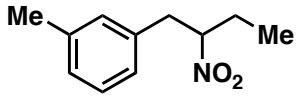
flask sequentially via syringe. The resulting suspension was heated in a 60 °C oil bath with rapid stirring for the indicated time. The reactor was cooled to rt, the flask was opened to air and the reaction mixture was diluted with diethyl ether (20 mL). The solution was washed twice with saturated ammonium chloride (25 mL) and once with brine (25 mL), dried over magnesium sulfate and concentrated *in vacuo*. The product was purified by silica gel flash chromatography.

General Protocol B. Synthesis of Nitroalkanes with Solid Benzyl Bromide Substrates: A hot 25 mL Schlenk flask equipped with magnetic stir bar and rubber septum was attached to a double manifold and cooled under vacuum. The flask was backfilled with N_2, the septum was removed, and CuBr (0.2 equiv), ligand **4** (0.25 equiv), base (1.2 equiv), and the benzyl bromide (1.0 equiv) were added. The septum was replaced, the flask was attached to a double manifold, and evacuated and backfilled with nitrogen five times. Anhydrous solvent (6 mL) and the nitroalkane (1.25 equiv) were added to the flask sequentially via syringe. The resulting suspension was heated in a 60 °C oil bath with rapid stirring for the indicated time. The reactor was cooled to rt, the flask was opened to air and the reaction mixture was diluted with diethyl ether (20 mL). The solution was washed twice with saturated ammonium chloride (25 mL) and once with brine (25 mL), dried over magnesium sulfate and concentrated *in vacuo*. The product was purified by silica gel flash chromatography.

5. Benzylation of Nitroalkanes.

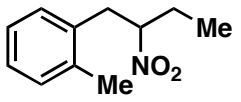


(**7**). According to general protocol A: CuBr (28.7 mg, 200 μmol), ligand **4** (76.6 mg, 250 μmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 μL, 1.25 mmol), and benzyl bromide (120 μL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **7** (153 mg, 85%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.34 – 7.23 (m, 3H), 7.20 – 7.12 (m, 2H), 4.63 (dddd, *J* = 9.7, 8.4, 5.9, 4.4 Hz, 1H), 3.26 (dd, *J* = 14.2, 8.6 Hz, 1H), 3.03 (dd, *J* = 14.2, 5.8 Hz, 1H), 2.03 (ddq, *J* = 14.5, 9.4, 7.3 Hz, 1H), 1.84 (dqd, *J* = 14.8, 7.5, 4.4 Hz, 1H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 135.8, 128.98, 128.95, 127.5, 91.5, 39.9, 27.0, 10.4; FTIR (cm^{-1}): 2975, 1549, 1456, 1374, 749, 699; GC/MS (EI) 179.2 $(M)^+$, 132.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{10}H_{13}NO_2]^+$: 179.0946; found: 179.0936.

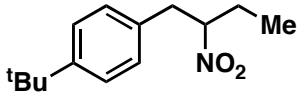


(**9**). According to general protocol A: CuBr (28.7 mg, 200 μmol), ligand **4** (76.6 mg, 250 μmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 μL, 1.25 mmol), and 3-methylbenzyl bromide (135 μL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **9** (164 mg, 85%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.20 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.6 Hz, 1H), 6.96 (d, *J* = 8.1 Hz, 2H), 4.62 (dddd, *J* = 9.7, 8.1, 5.9, 4.3 Hz, 1H), 3.23 (dd, *J* = 14.1, 8.5 Hz, 1H), 2.99 (dd, *J* = 14.1, 6.0 Hz, 1H), 2.33 (s, 3H), 2.02 (ddq, *J* = 14.6, 9.4, 7.3 Hz, 1H), 1.84 (dqd, *J* = 14.8, 7.5, 4.3 Hz, 1H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 138.6, 135.7, 129.8, 128.8, 128.2, 126.0, 91.6, 39.8, 27.0, 21.5, 10.4; FTIR (cm^{-1}): 2975, 2936, 1550, 1459, 1374, 782, 700; GC/MS (EI) 193.3

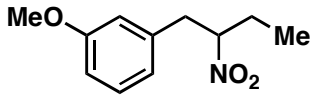
$(M)^+$, 146.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{11}H_{15}NO_2]^+$: 193.1103; found: 193.1086.



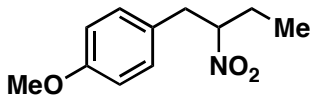
(**10**). According to general protocol A: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 2-methylbenzyl bromide (134 µL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **10** (164 mg, 85%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.19 – 7.11 (m, 3H), 7.08 (d, J = 6.8 Hz, 1H), 4.62 (dddd, J = 10.0, 8.3, 6.1, 4.3 Hz, 1H), 3.28 (dd, J = 14.4, 8.3 Hz, 1H), 3.06 (dd, J = 14.4, 6.2 Hz, 1H), 2.34 (s, 3H), 2.06 (ddq, J = 14.6, 9.6, 7.3 Hz, 1H), 1.84 (dqd, J = 14.8, 7.5, 4.3 Hz, 1H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 136.3, 134.0, 130.8, 129.8, 127.6, 126.5, 90.4, 37.3, 27.0, 19.5, 10.5; FTIR (cm^{-1}): 2974, 2937, 1550, 1458, 1373, 745; GC/MS (EI) 193.3 $(M)^+$, 146.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{11}H_{15}NO_2]^+$: 193.1103; found: 193.1111.



(**11**). According to general protocol A: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 4-(*tert*-butyl)benzyl bromide (184 µL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **11** (196 mg, 83%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.35 – 7.29 (m, 2H), 7.12 – 7.06 (m, 2H), 4.62 (dddd, *J* = 9.7, 8.6, 6.0, 4.4 Hz, 1H), 3.24 (dd, *J* = 14.2, 8.4 Hz, 1H), 2.99 (dd, *J* = 14.2, 6.0 Hz, 1H), 2.01 (ddq, *J* = 14.6, 9.4, 7.3 Hz, 1H), 1.84 (dqd, *J* = 14.8, 7.5, 4.3 Hz, 1H), 1.30 (s, 9H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 150.4, 132.7, 128.7, 125.9, 91.5, 39.4, 34.6, 31.4, 27.0, 10.4; FTIR (cm^{-1}): 2966, 2870, 1551, 1458, 1373; GC/MS (EI) 235.2 $(M)^+$, 188.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{14}H_{21}NO_2]^+$: 235.1572; found: 235.1557.

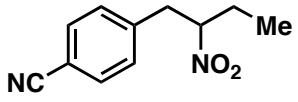


(**12**). According to general protocol A: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 3-methoxybenzyl bromide (140 µL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **12** (171 mg, 82%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.22 (t, *J* = 8.0 Hz, 1H), 6.80 (ddd, *J* = 8.3, 2.6, 0.8 Hz, 1H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.69 (t, *J* = 2.0 Hz, 1H), 4.63 (dddd, *J* = 9.7, 8.3, 6.0, 4.3 Hz, 1H), 3.79 (s, 3H), 3.24 (dd, *J* = 14.1, 8.5 Hz, 1H), 3.00 (dd, *J* = 14.1, 6.0 Hz, 1H), 2.01 (ddq, *J* = 14.6, 9.8, 7.3 Hz, 1H), 1.84 (dqd, *J* = 14.8, 7.5, 4.3 Hz, 1H), 0.98 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 159.9, 137.3, 130.0, 121.2, 114.8, 112.7, 91.4, 55.3, 39.9, 27.0, 10.4; FTIR (cm^{-1}): 2972, 2935, 1548, 1263, 1155, 1042, 781, 696; GC/MS (EI) 209.2 $(M)^+$, 162.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{11}H_{15}NO_3]^+$: 209.1052; found: 209.1058.

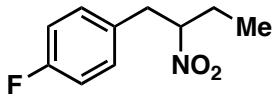


(**13**). According to general protocol A: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115

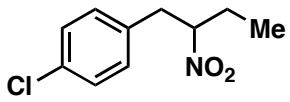
mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 4-methoxybenzyl bromide (146 µL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:2:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:2 hexanes : ethyl acetate) to afford nitroalkane **13** (141 mg, 67%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.07 (d, J = 8.7 Hz, 2H), 6.83 (d, J = 8.7 Hz, 2H), 4.58 (dddd, J = 9.7, 8.6, 5.8, 4.4 Hz, 1H), 3.78 (s, 3H), 3.19 (dd, J = 14.3, 8.6 Hz, 1H), 2.97 (dd, J = 14.3, 5.8 Hz, 1H), 2.07 – 1.94 (m, 1H), 1.83 (dqd, J = 14.8, 7.5, 4.3 Hz, 1H), 0.97 (t, J = 7.4 Hz, 3H) ; ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 158.9, 130.0, 127.7, 114.3, 91.8, 55.4, 39.1, 26.9, 10.4; FTIR (cm^{-1}): 2972, 1548, 1514, 1249, 1179, 1034; GC/MS (EI) 209.2 $(M)^+$, 162.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{11}H_{15}NO_3]^+$: 209.1052; found: 209.1057.



(**14**). According to general protocol B: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 4-cyanobenzyl bromide (196 mg, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:10:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:10 hexanes : ethyl acetate) to afford nitroalkane **14** (147 mg, 72%) as a white solid (97% pure with trace bibenzyl byproduct): mp = 40–41 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.60 (d, *J* = 8.1 Hz, 2H), 7.27 (d, *J* = 8.1 Hz, 2H), 4.63 (tt, *J* = 9.4, 4.8 Hz, 1H), 3.30 (dd, *J* = 14.4, 9.4 Hz, 1H), 3.08 (dd, *J* = 14.4, 5.0 Hz, 1H), 2.11 – 1.97 (m, 1H), 1.86 (dqd, *J* = 14.7, 7.4, 4.7 Hz, 1H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 141.2, 132.8, 129.8, 118.6, 111.6, 90.8, 39.6, 27.3, 10.3; FTIR (cm^{-1}): 2975, 2229, 1548, 1373, 863, 564; GC/MS (EI) 157.2 $(M–HNO_2)^+$. HRMS (CI) m/z, calculated for $[C_{11}H_{13}N_2O_2]^+$: 205.0977; found: 205.0982.

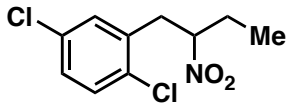


(**15**). According to general protocol A: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 4-fluorobenzyl bromide (125 µL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **15** (165 mg, 83%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.15 – 7.09 (m, 2H), 7.03 – 6.95 (m, 2H), 4.63 – 4.55 (m, 1H), 3.22 (dd, J = 14.3, 9.0 Hz, 1H), 3.01 (dd, J = 14.3, 5.5 Hz, 1H), 2.02 (ddq, J = 14.6, 9.4, 7.3 Hz, 1H), 1.84 (dqd, J = 14.8, 7.5, 4.4 Hz, 1H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 162.2 (d, *J* = 245.9 Hz), 131.5 (d, *J* = 3.3 Hz), 130.5 (d, *J* = 8.1 Hz), 115.9 (d, *J* = 21.4 Hz), 91.6, 39.0, 27.0, 10.4; ^{19}F NMR (376 MHz, $CDCl_3$) ∂ -115.0 – -115.2 (m); FTIR (cm^{-1}): 2975, 1550, 1373, 1224, 825; GC/MS (EI) 196.9 $(M)^+$, 150.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{10}H_{12}NO_2F]^+$: 197.0852; found: 197.0838.

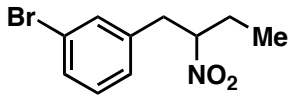


(**16**). According to general protocol B: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 4-chlorobenzyl bromide (206 mg, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica

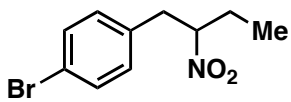
chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **16** (169 mg, 79%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.28 (d, J = 8.4 Hz, 2H), 7.09 (d, J = 8.4 Hz, 2H), 4.63 – 4.55 (m, 1H), 3.22 (dd, J = 14.3, 9.0 Hz, 1H), 3.00 (dd, J = 14.3, 5.5 Hz, 1H), 2.02 (ddq, J = 14.6, 9.4, 7.3 Hz, 1H), 1.84 (dqd, J = 14.8, 7.5, 4.4 Hz, 1H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 134.2, 133.5, 130.3, 129.1, 91.3, 39.1, 27.0, 10.4; FTIR (cm^{-1}): 2975, 1549, 1493, 1374, 1094, 1016, 805; GC/MS (EI) 166.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{10}H_{12}NO_2Cl]^+$: 213.0556; found: 213.0546.



(**17**). According to general protocol B: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 2,5-dichlorobenzyl bromide (240 mg, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **17** (207 mg, 84%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.31 (d, J = 8.5 Hz, 1H), 7.20 (dd, J = 8.5, 2.5 Hz, 1H), 7.16 (d, J = 2.5 Hz, 1H), 4.75 (ddd, J = 14.0, 9.0, 5.1 Hz, 1H), 3.30 – 3.17 (m, 2H), 2.13 – 2.01 (m, 1H), 1.95 – 1.82 (m, 1H), 1.02 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 135.3, 133.1, 132.4, 131.3, 131.0, 129.3, 89.1, 37.3, 27.4, 10.4; FTIR (cm^{-1}): 2975, 1550, 1471, 1373, 1098, 815; GC/MS (EI) 247.2 $(M)^+$, 200.1 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{10}H_{11}NO_2Cl_2]^+$: 247.0167; found: 247.0148.

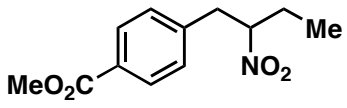


(**18**). According to general protocol B: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), 3-bromobenzyl bromide (250 mg, 1.0 mmol), anhydrous hexanes (6 mL) and 1-nitropropane (112 µL, 1.25 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **18** (212 mg, 82%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.40 (ddd, *J* = 8.0, 1.7, 1.2 Hz, 1H), 7.32 (t, *J* = 1.7 Hz, 1H), 7.18 (t, *J* = 7.8 Hz, 1H), 7.12 – 7.05 (m, 1H), 4.66 – 4.56 (m, 1H), 3.23 (dd, *J* = 14.3, 8.9 Hz, 1H), 3.00 (dd, *J* = 14.3, 5.5 Hz, 1H), 2.02 (ddq, *J* = 14.6, 9.3, 7.3 Hz, 1H), 1.84 (dqd, *J* = 14.8, 7.5, 4.5 Hz, 1H), 0.99 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 138.0, 132.0, 130.7, 130.5, 127.6, 122.9, 91.1, 39.3, 27.1, 10.4; FTIR (cm^{-1}): 2975, 1549, 1374, 1073, 780, 693; GC/MS (EI) 257.1 $(M)^+$, 210.1 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{10}H_{12}NO_2Br]^+$: 257.0051; found: 257.0057.

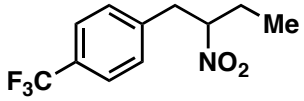


(**19**). According to general protocol B: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 4-bromobenzyl bromide (250 mg, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **19** (210 mg, 81%) as a white solid: mp = 55–56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.43 (d, J = 8.4 Hz, 2H), 7.03 (d, J = 8.3 Hz, 2H), 4.64 – 4.54 (m, 1H), 3.21 (dd, J = 14.3, 9.0 Hz, 1H), 2.99 (dd, J = 14.3, 5.5 Hz, 1H), 2.02 (ddq, J = 14.6, 9.4, 7.3 Hz, 1H), 1.84 (dqd, J =

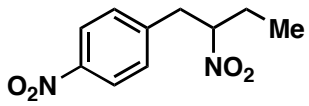
14.9, 7.6, 4.4 Hz, 1H), 0.99 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 134.7, 132.1, 130.7, 121.6, 91.2, 39.2, 27.1, 10.4; FTIR (cm^{-1}): 2974, 1549, 1489, 1373, 1073, 1012, 801; GC/MS (EI) 257.0 $(M)^+$, 210.1 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{10}H_{12}NO_2Br]^+$: 257.0051; found: 257.0067.



(**20**). According to general protocol B: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium methoxide (64.8 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and methyl 4-(bromomethyl)benzoate (229 mg, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:5:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:5 hexanes : ethyl acetate) to afford nitroalkane **20** (206 mg, 87%) as a clear oil (96% pure with trace bibenzyl byproduct): ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.98 (d, J = 8.3 Hz, 2H), 7.24 (d, J = 8.3 Hz, 2H), 4.69 – 4.60 (m, 1H), 3.92 (s, 3H), 3.31 (dd, J = 14.2, 9.0 Hz, 1H), 3.09 (dd, J = 14.2, 5.5 Hz, 1H), 2.04 (ddq, J = 14.6, 9.3, 7.3 Hz, 1H), 1.85 (dqd, J = 14.8, 7.5, 4.5 Hz, 1H), 1.00 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 167.2, 141.1, 130.3, 129.3, 129.1, 91.0, 52.4, 39.6, 27.1, 10.4; FTIR (cm^{-1}): 2953, 1721, 1550, 1436, 1282, 1181, 1111; GC/MS (EI) 190.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{12}H_{15}NO_4]^+$: 237.1001; found: 237.1020.

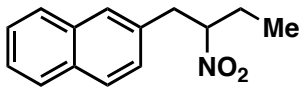


(**21**). According to general protocol A: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 4-(trifluoromethyl)benzyl bromide (155 µL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 24 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **21** (200 mg, 81%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.57 (d, J = 8.1 Hz, 2H), 7.28 (d, J = 8.0 Hz, 2H), 4.69 – 4.60 (m, 1H), 3.32 (dd, J = 14.3, 9.1 Hz, 1H), 3.09 (dd, J = 14.3, 5.3 Hz, 1H), 2.05 (ddq, J = 14.6, 9.3, 7.3 Hz, 1H), 1.87 (dqd, J = 14.8, 7.5, 4.5 Hz, 1H), 1.01 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 139.8 (q, *J* = 1.1 Hz), 130.1 (q, *J* = 32.7 Hz), 129.4, 125.9 (q, *J* = 3.8 Hz), 124.1 (q, *J* = 272.4 Hz), 91.0, 39.4, 27.2, 10.4; ^{19}F NMR (376 MHz, $CDCl_3$) ∂ –62.6 (s); FTIR (cm^{-1}): 1549, 1326, 1161, 1123, 1068, 863; GC/MS (EI) 200.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{11}H_{11}F_3]^+$: 200.0813; found: 200.0821.

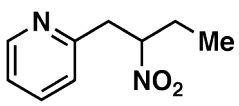


(**22**). According to general protocol B: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 4-nitrobenzyl bromide (216 mg, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:5:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:5 hexanes : ethyl acetate) to afford nitroalkane **22** (163 mg, 72%) as a clear oil (97% pure with trace bibenzyl byproduct): ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 8.16 (d, J = 8.6 Hz, 2H), 7.34 (d, J = 8.7 Hz, 2H), 4.67 (tt, J = 9.4, 4.7 Hz, 1H), 3.36 (dd, J = 14.4, 9.6 Hz, 1H), 3.14 (dd, J = 14.4, 4.9 Hz, 1H), 2.07 (ddq, J = 14.6, 9.3, 7.3 Hz, 1H), 1.90 (dqd, J = 14.8, 7.4, 4.6 Hz, 1H), 1.01 (t, J = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 147.4, 143.2, 129.9, 124.2, 90.7, 39.3, 27.3, 10.3; FTIR (cm^{-1}): 2976, 1606, 1549, 1520, 1348, 870; GC/MS (EI)

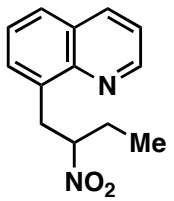
224.1 $(M)^+$, 177.2 $(M–HNO_2)^+$. HRMS (CI) m/z, calculated for $[C_{10}H_{13}N_2O_4]^+$: 225.0875; found: 225.0877.



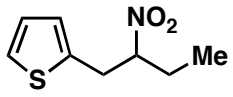
(**23**). According to general protocol B: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 2-(bromomethyl)naphthalene (221 mg, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 24 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:1 hexanes : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **23** (164 mg, 72%) as a yellow solid: mp = 59–60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) *∂* 7.84 – 7.76 (m, 3H), 7.62 (s, 1H), 7.52 – 7.44 (m, 2H), 7.28 (dd, *J* = 8.4, 1.7 Hz, 1H), 4.74 (dddd, *J* = 9.8, 8.6, 6.0, 4.3 Hz, 1H), 3.44 (dd, *J* = 14.2, 8.5 Hz, 1H), 3.20 (dd, *J* = 14.2, 5.9 Hz, 1H), 2.08 (ddq, *J* = 14.6, 9.4, 7.3 Hz, 1H), 1.89 (dqd, *J* = 14.9, 7.5, 4.3 Hz, 1H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *∂* 133.5, 133.2, 132.6, 128.7, 127.9, 127.79, 127.78, 126.8, 126.5, 126.1, 91.4, 40.0, 27.0, 10.4; FTIR (cm^{-1}): 2974, 1545, 1521, 1373, 817, 749; GC/MS (EI) 229.2 $(M)^+$, 182.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{14}H_{15}NO_2]^+$: 229.1103; found: 229.1118.



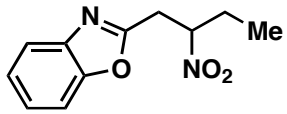
(**24**). According to general protocol B: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (211 mg, 2.2 mmol), anhydrous benzene (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 2-(bromomethyl)pyridine hydrobromide (253 mg, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 24 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography using 5-20 µm silica gel (100:10 hexanes : ethyl acetate**)** to afford nitroalkane **24** (134 mg, 74%) as a pale yellow oil: ^{1}H NMR (400 MHz, $CDCl_3$) *∂* 8.54 (d, *J* = 4.0 Hz, 1H), 7.61 (td, *J* = 7.7, 1.5 Hz, 1H), 7.20 – 7.10 (m, 2H), 5.03 (tt, *J* = 9.3, 4.8 Hz, 1H), 3.44 (dd, *J* = 14.6, 9.3 Hz, 1H), 3.17 (dd, *J* = 14.6, 4.8 Hz, 1H), 2.05 (tt, *J* = 15.5, 7.4 Hz, 1H), 1.92 (dp, *J* = 14.6, 7.5, 5.0 Hz, 1H), 1.01 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *∂* 156.1, 149.8, 136.9, 123.8, 122.4, 89.4, 41.2, 27.4, 10.3; FTIR (cm^{-1}): 2974, 1592, 1549, 1476, 1439, 1375, 759; GC/MS (EI) 134.1 $(M–NO_2)^+$. HRMS (CI) m/z, calculated for $[C_9H_{13}N_2O_2]^+$: 181.0977; found: 181.0982.



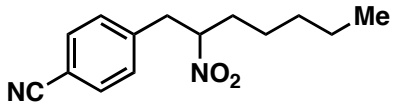
(**25**). According to general protocol B: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitropropane (112 µL, 1.25 mmol), and 8-(bromomethyl)-quinoline (222 mg, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 24 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography using 5-20 µm silica gel (50:50 benzene : petroleum ether) to afford nitroalkane **25** (157 mg, 68%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) *∂* 8.91 (dd, *J* = 4.2, 1.7 Hz, 1H), 8.15 (dd, *J* = 8.3, 1.5 Hz, 1H), 7.74 (dd, *J* = 8.1, 1.4 Hz, 1H), 7.50 (d, *J* = 6.3 Hz, 1H), 7.47 – 7.39 (m, 2H), 5.14 (tt, *J* = 9.3, 4.5 Hz, 1H), 3.94 (dd, *J* = 13.6, 4.6 Hz, 1H), 3.56 (dd, *J* = 13.6, 9.6 Hz, 1H), 2.13 (ddq, *J* = 14.6, 9.4, 7.3 Hz, 1H), 1.99 (dqd, *J* = 14.7, 7.5, 4.4 Hz, 1H), 1.02 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) *∂* 149.8, 146.6, 136.6, 134.5, 130.5, 128.5, 127.9, 126.4, 121.4, 91.0, 36.5, 27.7, 10.5; FTIR (cm^{-1}): 2970, 1547, 1499, 1373, 858, 794; GC/MS (EI) 230.1 $(M)^+$, 184.1 $(M–NO_2)^+$. HRMS (EI) m/z, calculated for $[C_{13}H_{14}N_2O_2]^+$: 230.1055; found: 230.1046.



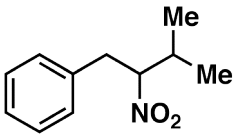
(**26**). According to general protocol A: CuBr (28.7 mg, 200 μmol), ligand **4** (76.6 mg, 250 μmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous dioxane (6 mL), 1-nitropropane (112 μL, 1.25 mmol), and 2-(bromomethyl)thiophene (110 μL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 24 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:2:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:2 hexanes : ethyl acetate) to afford nitroalkane **26** (80 mg, 43%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.19 (dd, *J* = 5.2, 1.1 Hz, 1H), 6.94 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.86 – 6.82 (m, 1H), 4.69 – 4.59 (m, 1H), 3.51 (dd, *J* = 15.2, 8.6 Hz, 1H), 3.24 (dd, *J* = 15.2, 5.5 Hz, 1H), 2.02 (ddq, *J* = 14.7, 9.1, 7.3 Hz, 1H), 1.89 (dqd, *J* = 14.8, 7.5, 4.5 Hz, 1H), 1.00 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 137.3, 127.3, 126.8, 125.0, 91.3, 33.7, 26.9, 10.3; FTIR (cm^{-1}): 2974, 1550, 1440, 1374, 858, 703; GC/MS (EI) 185.1 $(M)^+$, 138.1 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_8H_{11}NO_2S]^+$: 185.0511; found: 185.0517.



(**27**). According to general procedure A: CuBr (28.7 mg, 200 μmol), ligand **4** (76.6 mg, 250 μmol), sodium trimethylsilanolate (135 mg, 1.2 mmol), anhydrous benzene (6 mL), 1-nitropropane (112 μL, 1.25 mmol), and melted 2-bromomethyl-benzooxazole (132 μL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography using 5-20 μm silica gel (100:7:1 hexanes : diethyl ether : trifluoroacetic acid → 100:7 hexanes : diethyl ether) to afford nitroalkane **27** (183 mg, 83%) as a pale yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) ∂ 7.74 – 7.70 (m, 1H), 7.55 – 7.51 (m, 1H), 7.40 – 7.35 (m, 2H), 5.07 (ddd, *J* = 13.6, 8.6, 5.1 Hz, 1H), 3.77 (dd, *J* = 16.3, 8.8 Hz, 1H), 3.45 (dd, *J* = 16.3, 5.0 Hz, 1H), 2.18 – 2.09 (m, 1H), 2.09 – 2.01 (m, 1H), 1.07 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) ∂ 162.4, 150.7, 139.7, 125.9, 125.2, 119.7, 111.0, 85.9, 31.7, 27.3, 10.0; FTIR (cm^{-1}): 2975, 1575, 1509, 1241, 1159, 747; GC/MS (CI) 174.1 $(M–NO_2)^+$. HRMS (CI) m/z, calculated for $[C_{11}H_{13}N_2O_3]^+$: 221.0926; found: 221.0929.

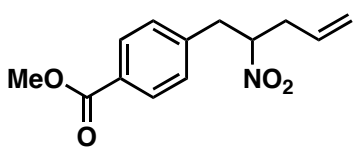


(**28**). According to general protocol B: CuBr (28.7 mg, 200 μmol), ligand **4** (76.6 mg, 250 μmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 1-nitrohexane (174 μL, 1.25 mmol), and 4-cyanobenzyl bromide (196 mg, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 24 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:8:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:8 hexanes : ethyl acetate) to afford nitroalkane **28** (176 mg, 71%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.61 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 2H), 4.69 (tt, *J* = 9.5, 4.7 Hz, 1H), 3.30 (dd, *J* = 14.4, 9.5 Hz, 1H), 3.08 (dd, *J* = 14.4, 4.9 Hz, 1H), 2.10 – 1.98 (m, 1H), 1.83 – 1.71 (m, 1H), 1.41 – 1.23 (m, 6H), 0.91 – 0.84 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 141.2, 132.8, 129.8, 118.6, 111.6, 89.5, 39.9, 33.9, 31.1, 25.5, 22.4, 14.0; FTIR (cm^{-1}): 2957**,** 2930, 2229, 1550, 1506, 565; GC/MS (EI) 199.3 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{14}H_{19}N_2O_2]^+$: 247.1447; found: 247.1443.

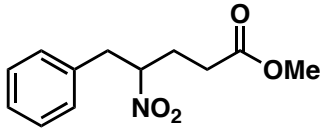


(**29**). CuBr (28.7 mg, 200 μmol), ligand **4** (76.6 mg, 250 μmol), and sodium *tert*-butoxide (115 mg, 1.2 mmol) were added to a 25 mL Schlenk flask equipped with stir bar. The flask was sealed with a rubber septum, attached to a double manifold, and evacuated and

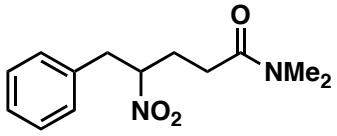
backfilled with nitrogen five times. Anhydrous dioxane (6 mL) was added and the resulting mixture was heated in a 60 °C oil bath with rapid stirring for 5 h. 2-methyl-1-nitropropane (135 µL, 1.25 mmol) and benzyl bromide (120 µL, 1.0 mmol) were then added and the resulting viscous mixture was allowed to continue heating at 60 °C with rapid stirring for 24 h. The flask was then cooled to rt, opened to air, and the reaction mixture was diluted with diethyl ether (20 mL). The solution was washed twice with saturated ammonium chloride (25 mL) and once with brine (25 mL), dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **29** (126 mg, 65%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.33 – 7.22 (m, 3H), 7.17 – 7.13 (m, 2H), 4.50 (ddd, *J* = 11.0, 7.4, 3.9 Hz, 1H), 3.21 (dd, *J* = 14.5, 10.6 Hz, 1H), 3.10 (dd, *J* = 14.5, 3.9 Hz, 1H), 2.31 – 2.17 (m, 1H), 1.11 (d, *J* = 6.8 Hz, 3H), 1.05 (d, *J* = 6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 136.2, 128.9, 128.8, 127.4, 96.2, 37.2, 32.4, 19.2, 18.9; FTIR (cm^{-1}): 2971, 1548, 1456, 1374, 699; GC/MS (EI) 146.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{11}H_{15}NO_2]^+$: 193.1103; found: 193.1084.



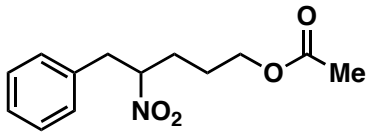
(**30**). According to general protocol B: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium methoxide (64.8 mg, 1.2 mmol), anhydrous hexanes (6 mL), 4-nitro-1-butene (128 µL, 1.25 mmol), and methyl 4-(bromomethyl)benzoate (229 mg, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 24 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:3:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:3 hexanes : ethyl acetate) to afford nitroalkane **30** (179 mg, 72%) as a white solid: mp = 52–53 °C; ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.98 (d, *J* = 8.3 Hz, 2H), 7.24 (d, *J* = 8.2 Hz, 2H), 5.78 – 5.66 (m, 1H), 5.22 – 5.14 (m, 2H), 4.76 (tt, *J* = 8.8, 5.3 Hz, 1H), 3.91 (s, 3H), 3.32 (dd, *J* = 14.3, 9.0 Hz, 1H), 3.12 (dd, *J* = 14.3, 5.4 Hz, 1H), 2.78 – 2.68 (m, 1H), 2.61 – 2.53 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 166.9, 140.7, 131.1, 130.3, 129.5, 129.1, 120.3, 88.8, 52.4, 39.2, 37.8; FTIR (cm^{-1}): 2953, 1721, 1552, 1436, 1282, 1182, 1112, 764**;** GC/MS (EI) 202.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{13}H_{15}NO_4]^+$: 249.1001; found: 249.0994.



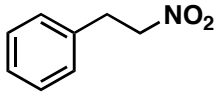
(**31**). According to general protocol A: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium methoxide (64.8 mg, 1.2 mmol), anhydrous hexanes (6 mL), methyl 4-nitrobutyrate (160 µL, 1.25 mmol), and benzyl bromide (120 µL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 6 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:5:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:5 hexanes : ethyl acetate) to afford nitroalkane **31** (150 mg, 63%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.35 – 7.24 (m, 3H), 7.16 (d, J = 7.1 Hz, 2H), 4.86 – 4.74 (m, 1H), 3.69 (s, 3H), 3.29 (dd, J = 14.2, 8.4 Hz, 1H), 3.07 (dd, J = 14.2, 5.9 Hz, 1H), 2.49 – 2.11 (m, 4H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 172.7, 135.2, 129.02, 128.99, 127.7, 88.8, 52.2, 40.2, 30.1, 28.3; FTIR (cm^{-1}): 1734, 1550, 1437, 1364, 1202, 701; GC/MS (EI) 190.2 $(M–HNO_2)^+$. HRMS (CI) m/z, calculated for $[C_{12}H_{16}NO_4]^+$: 238.1079; found: 238.1084.



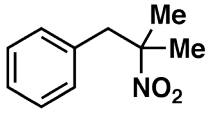
(**32**). According to general protocol A: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous dioxane (6 mL), N,N-dimethyl-4-nitro-butanamide (181 µL, 1.25 mmol), and benzyl bromide (120 µL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 24 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (50:50:1 hexanes : ethyl acetate : trifluoroacetic acid → 50:50 hexanes : ethyl acetate) to afford nitroalkane **32** (194 mg, 77%) as a green oil: ^{1}H NMR (400 MHz, DMSO) ∂ 7.33 – 7.16 (m, 5H), 5.00 – 4.90 (m, 1H), 3.15 (qd, *J* = 14.3, 7.2 Hz, 2H), 2.89 (s, 3H), 2.79 (s, 3H), 2.38 – 2.30 (m, 2H), 2.11 – 2.03 (m, 2H); ^{13}C NMR (101 MHz, DMSO) ∂ 170.1, 135.9, 128.7, 128.4, 126.9, 88.9, 36.3, 34.7, 28.5, 28.2; FTIR (cm^{-1}): 1653, 1549, 1200, 1147, 701; GC/MS (CI) 251.2 $(M+H)^+$ 204.2 $(M–NO_2)^+$. HRMS (CI) m/z, calculated for $[C_{13}H_{19}N_2O_3]^+$: 251.1396; found: 251.1403.



(**33**). According to general protocol A: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous hexanes (6 mL), 4-nitrobutyl acetate (175 µL, 1.25 mmol), and benzyl bromide (120 µL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 24 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:5:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:5 hexanes : ethyl acetate) to afford nitroalkane **33** (171 mg, 68%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.35 – 7.25 (m, 3H), 7.18 – 7.13 (m, 2H), 4.73 (dddd, *J* = 9.9, 8.6, 6.1, 4.0 Hz, 1H), 4.15 – 4.02 (m, 2H), 3.28 (dd, *J* = 14.1, 8.4 Hz, 1H), 3.04 (dd, *J* = 14.1, 6.0 Hz, 1H), 2.16 – 2.02 (m, 4H), 1.92 – 1.80 (m, 1H), 1.75 – 1.64 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 172.3, 135.3, 129.03, 128.98, 127.7, 89.5, 63.7, 40.2, 30.0, 25.0, 21.0; FTIR (cm^{-1}): 1734**,** 1550, 1507, 1457, 1240, 668; GC/MS (EI) 204.2 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{13}H_{18}NO_4]^+$: 252.1236; found: 252.1250.

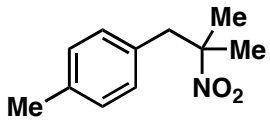


(**34**). According to general protocol A: CuBr (28.7 mg, 200 µmol), ligand **4** (61.3 mg, 200 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous dioxane (6 mL), nitromethane (403 µL, 7.5 mmol), and benzyl bromide (120 µL, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 4 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography (100:2:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:2 hexanes : ethyl acetate) to afford nitroalkane **34** (110 mg, 73%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.40 – 7.25 (m, 3H), 7.24 – 7.17 (m, 2H), 4.62 (t, *J* = 7.4 Hz, 2H), 3.33 (t, *J* = 7.4 Hz, 2H); ^{13}C NMR (151 MHz, $CDCl_3$) ∂ 135.8, 129.1, 128.7, 127.6, 76.4, 33.6; FTIR (cm^{-1}): 3032, 1551, 1497, 1456, 1378, 699**;** GC/MS (EI) 151.1 $(M)^+$. HRMS (EI) m/z, calculated for $[C_8H_9O_2N]^+$: 151.0633; found: 151.0629.

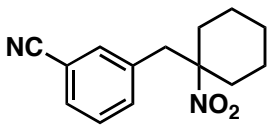


(**35**). CuBr (86.1 mg, 600 µmol), ligand **4** (184 mg, 600 µmol), and sodium *tert*-butoxide (346 mg, 3.6 mmol) were added to a 50 mL Schlenk flask equipped with stir bar. The flask was sealed with a rubber septum, attached to a double manifold, and evacuated and backfilled with nitrogen five times. Anhydrous cyclohexane (15 mL) was added and the resulting mixture was heated in a 60 °C oil bath with rapid stirring for 1 h. 2-Nitropropane (310 µL, 3.45 mmol) and benzyl bromide (359 µL, 3.0 mmol) were then added and the

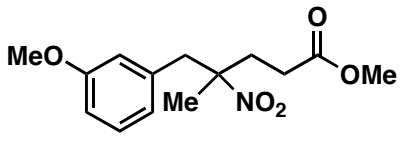
resulting viscous mixture was allowed to continue heating at 60 °C with rapid stirring for 48 h. The flask was then cooled to rt, opened to air, and the reaction mixture was diluted with diethyl ether (60 mL). The solution was washed twice with saturated ammonium chloride (75 mL) and once with brine (75 mL), dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **35** (394 mg, 73%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.33 – 7.27 (m, 3H), 7.13 – 7.09 (m, 2H), 3.20 (s, 2H), 1.58 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 135.0, 130.2, 128.6, 127.6, 88.8, 46.9, 25.7; FTIR (cm^{-1}): 2990, 1538, 1456, 1397, 1349, 702; GC/MS (EI) 179.1 $(M)^+$, 132.1 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{10}H_{13}NO_2]^+$: 179.0946; found: 179.0937.



(**36**). CuBr (86.1 mg, 600 µmol), ligand **4** (184 mg, 600 µmol), and sodium *tert*-butoxide (346 mg, 3.6 mmol) were added to a 50 mL Schlenk flask equipped with stir bar. The flask was sealed with a rubber septum, attached to a double manifold, and evacuated and backfilled with nitrogen five times. Anhydrous cyclohexane (15 mL) was added and the resulting mixture was heated in a 60 °C oil bath with rapid stirring for 1 h. 2-Nitropropane (310 µL, 3.45 mmol) and 4-methylbenzyl bromide (419 µL, 3.0 mmol) were then added and the resulting viscous mixture was allowed to continue heating at 60 °C with rapid stirring for 48 h. The flask was then cooled to rt, opened to air, and the reaction mixture was diluted with diethyl ether (60 mL). The solution was washed twice with saturated ammonium chloride (75 mL) and once with brine (75 mL), dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by flash silica chromatography (100:1:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:1 hexanes : ethyl acetate) to afford nitroalkane **36** (409 mg, 71%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.10 (d, J = 7.7 Hz, 2H), 6.99 (d, J = 8.0 Hz, 2H), 3.15 (s, 2H), 2.32 (s, 3H), 1.56 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 137.3, 132.0, 130.1, 129.3, 88.8, 46.5, 25.7, 21.2; FTIR (cm^{-1}): 2988, 2925, 1539, 1516, 1396, 1372, 1348, 793; GC/MS (EI) 193.1 $(M)^+$, 146.1 $(M–HNO_2)^+$. HRMS (EI) m/z, calculated for $[C_{11}H_{15}NO_2]^+$: 193.1103; found: 193.1097.

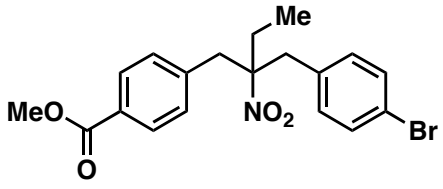


(**37**). According to general protocol B: CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium *tert*-butoxide (115 mg, 1.2 mmol), anhydrous dioxane (6 mL), nitrocyclohexane (154 µL, 1.25 mmol), and 3-cyanobenzyl bromide (196 mg, 1.0 mmol) were combined under N_2 and heated at 60 °C with rapid stirring for 24 h. The reaction was worked up according to the general protocol and purified by flash silica chromatography using 5-20 µm silica gel (5% EtOAc in hexanes with 0.1M trifluoroacetic acid) to afford nitroalkane **37** (178 mg, 73%) as a white solid: mp = 63–64 °C; ^{1}H NMR (600 MHz, $CDCl_3$) ∂ 7.57 (d, J = 7.7 Hz, 1H), 7.40 (t, J = 7.8 Hz, 1H), 7.35 (s, 1H), 7.27 (d, J = 8.7 Hz, 1H), 3.12 (s, 2H), 2.38 (d, J = 13.3 Hz, 2H), 1.71 – 1.58 (m, 5H), 1.45 – 1.35 (m, 2H), 1.35 – 1.28 (m, 1H); ^{13}C NMR (151 MHz, $CDCl_3$) ∂ 135.8, 134.4, 133.4, 131.4, 129.5, 118.6, 112.6, 91.7, 46.3, 34.0, 24.7, 22.3; FTIR (cm^{-1}): 2940, 2230, 1535, 1449, 1345, 692; GC/MS (EI) 198.2 $(M–NO_2)^+$. HRMS (CI) m/z, calculated for $[C_{14}H_{17}N_2O_2]^+$: 245.1290; found: 245.1284.

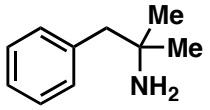


(**38**). In a nitrogen glovebox, CuBr (14.3 mg, 100 µmol), ligand **4** (38.3 mg, 125 µmol), sodium trimethylsilanolate (67.3 mg, 600 µmol), and anhydrous cyclohexane (3 mL) were added to a dry threaded 16

mm test tube equipped with a stir bar. The tube was sealed with a Telfon lined cap and heated in an aluminum block on a temperature controlled stir plate to 60°C with vigorous stirring for 1 hour. After the allotted time, the reaction was removed from the aluminum block and allowed to cool to rt. Once cooled, methyl 4-nitropentanoate (82 µL, 575 µmol) and 3-methoxybenzyl bromide (70 µL, 500 µmol) were added to the reaction vessel. The reaction was returned to the aluminum block and heated to 60 °C with rapid stirring for 24 h. The reaction was then removed from the glovebox, allowed to cool to rt, and exposed to air. The solution was diluted with diethyl ether (10 mL), washed twice with saturated ammonium chloride (10 mL), and once with brine (10 mL). The organic layer was dried with magnesium sulfate and concentrated *in vacuo*. The crude product was purified by flash silica chromatography (100:3:1 hexanes : ethyl acetate : trifluoroacetic acid → 100:3 hexanes : ethyl acetate) to afford nitroalkane **38** (74.5 mg, 53%) as a yellow oil: ^{1}H NMR (600 MHz, $CDCl_3$) ∂ 7.21 (t, *J* = 7.9 Hz, 1H), 6.82 (dd, *J* = 8.3, 2.5 Hz, 1H), 6.67 (d, *J* = 7.5 Hz, 1H), 6.63 (s, 1H), 3.78 (s, 3H), 3.69 (s, 3H), 3.33 (d, *J* = 13.9 Hz, 1H), 3.03 (d, *J* = 13.9 Hz, 1H), 2.53 – 2.46 (m, 1H), 2.42 – 2.26 (m, 2H), 2.16 – 2.10 (m, 1H), 1.48 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) ∂ 172.6, 159.6, 135.7, 129.6, 122.4, 115.9, 112.9, 91.0, 55.2, 52.0, 46.2, 34.2, 28.9, 21.3; FTIR (cm^{-1}): 2870, 1734, 1540, 1507, 1457, 1143; GC/MS (CI) 281.1 $(M)^+$, 235.1 $(M–NO_2)^+$. HRMS (CI) m/z, calculated for $[C_{14}H_{19}NO_5]^+$: 281.1263; found: 281.1257.



(**39**). CuBr (28.7 mg, 200 µmol), ligand **4** (76.6 mg, 250 µmol), sodium methoxide (64.8 mg, 1.2 mmol), nitroalkane **19** (323 mg, 1.25 mmol), and methyl 4-(bromomethyl)benzoate (229 mg, 1.0 mmol) were added to a 25 mL Schlenk flask equipped with stir bar. The flask was sealed with a rubber septum, attached to a double manifold, and evacuated and backfilled with nitrogen five times. Anhydrous dioxane (6 mL) was added and the resulting mixture was heated in a 60 °C oil bath with rapid stirring for 48 h. The flask was then cooled to rt, opened to air, and the reaction mixture was diluted with diethyl ether (20 mL). The solution was washed twice with saturated ammonium chloride (25 mL) and once with brine (25 mL), dried over magnesium sulfate and concentrated *in vacuo*. The crude product was purified by flash silica chromatography (70:30:1 petroleum ether : benzene : trifluoroacetic acid → 60:40 petroleum ether : benzene). The resulting residue was washed with hexanes to afford nitroalkane **39** (264 mg, 65%) as a white solid: mp = 92–93 °C; ^{1}H NMR (600 MHz, $CDCl_3$) ∂ 7.97 (d, *J* = 8.3 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.17 (d, *J* = 8.2 Hz, 2H), 6.97 (d, *J* = 8.3 Hz, 2H), 3.91 (s, 3H), 3.44 (d, *J* = 14.4 Hz, 1H), 3.36 (d, *J* = 14.5 Hz, 1H), 3.21 (d, *J* = 14.4 Hz, 1H), 3.13 (d, *J* = 14.5 Hz, 1H), 1.81 (q, *J* = 7.4 Hz, 2H), 1.09 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) ∂ 166.8, 139.8, 133.5, 132.0, 131.7, 130.1, 130.0, 129.8, 122.0, 95.7, 52.3, 42.1, 41.7, 25.5, 9.0; FTIR (cm^{-1}): 2949, 1719, 1539, 1281, 1110; GC/MS (CI) 406.1 $(M)^+$, 359.1 $(M–HNO_2)^+$**.** HRMS (CI) m/z, calculated for $[C_{19}H_{20}NO_4Br]^+$: 405.0576; found: 405.0590.



(**40**). Nitroalkane **35** (179 mg, 1.0 mmol) and methanol were added to a 25 mL recovery flask equipped with stir bar. Using a T joint adapter the flask was evacuated and backfilled with nitrogen several times. The adapter was removed and Palladium on carbon was quickly added. The adapter was replaced and the flask was evacuated and backfilled five times with nitrogen. A hydrogen balloon was added to the T joint and the flask was evacuated and backfilled ten times with hydrogen. The resulting suspension was heated in a 40 °C oil bath for 24 h. The flask was then cooled to rt, vented, and the suspension was poured

through a fritted funnel with celite. The solution was concentrated *in vacuo* to afford amine **40** (146 mg, 98%) as a clear oil: ^{1}H NMR (400 MHz, $CDCl_3$) ∂ 7.34 – 7.15 (m, 5H), 2.66 (s, 2H), 1.26 (s, 2H), 1.12 (s, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) ∂ 138.5, 130.5, 128.0, 126.3, 51.1, 50.1, 30.4; FTIR (cm^{-1}): 2962, 1452, 1386, 1381, 854, 724, 702; ESI+ 150.0 $(M+H)^+$. HRMS (QTOF) m/z, calculated for $[C_{10}H_{16}N]^+$: 150.1283; found: 150.1281.

6. References.

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.

(2) Budzelaar, P. H. M.; Moonen, N. N. P.; de Gelder, R.; Smits, J. M. M.; Gal, A. W. *Eur. J. Inorg. Chem.* **2000**, *2000*, 753.

(3) Dwyer, A. N.; Grossel, M. C.; Horton, P. N. *Supramol. Chem.* **2004**, *16*, 405.

(4) Prazeres, V. F. V.; Tizon, L.; Otero, J. M.; Guardado-Calvo, P.; Llamas-Saiz, A. L.; van Raaij, M. J.; Castedo, L.; Lamb, H.; Hawkins, A. R.; Gonzalez-Bello, C. *J. Med. Chem.* **2010**, *53*, 191.

(5) Anthony, N. G.; Breen, D.; Clarke, J.; Donoghue, G.; Drummond, A. J.; Ellis, E. M.; Gemmell, C. G.; Helesbeux, J.-J.; Hunter, I. S.; Khalaf, A. I.; Mackay, S. P.; Parkinson, J. A.; Suckling, C. J.; Waigh, R. D. *J. Med. Chem.* **2007**, *50*, 6116.

(6) Skiles, J. W.; Fuchs, V.; Miao, C.; Sorcek, R.; Grozinger, K. G.; Mauldin, S. C.; Vitous, J.; Mui, P. W.; Jacober, S.; Chow, G.; Matteo, M.; Skoog, M.; Weldon, S. M.; Possanza, G.; Keirns, J.; Letts, G.; Rosenthal, A. S. *J. Med. Chem.* **1992**, *35*, 641.

(7) Marsh, G. P.; Parsons, P. J.; McCarthy, C.; Corniquet, X. G. *Org. Lett.* **2007**, *9*, 2613.

(8) Bobál, P.; Lightner, D. A. *J. Heterocycl. Chem.* **2001**, *38*, 527.

(9) Zhang, H.-Z.; Zhang, H.; Kemnitzer, W.; Tseng, B.; Cinatl, J.; Michaelis, M.; Doerr, H. W.; Cai, S. X. *J. Med. Chem.* **2006**, *49*, 1198.

(10) Ballini, R.; Barboni, L.; Giarlo, G. *J. Org. Chem.* **2004**, *69*, 6907.

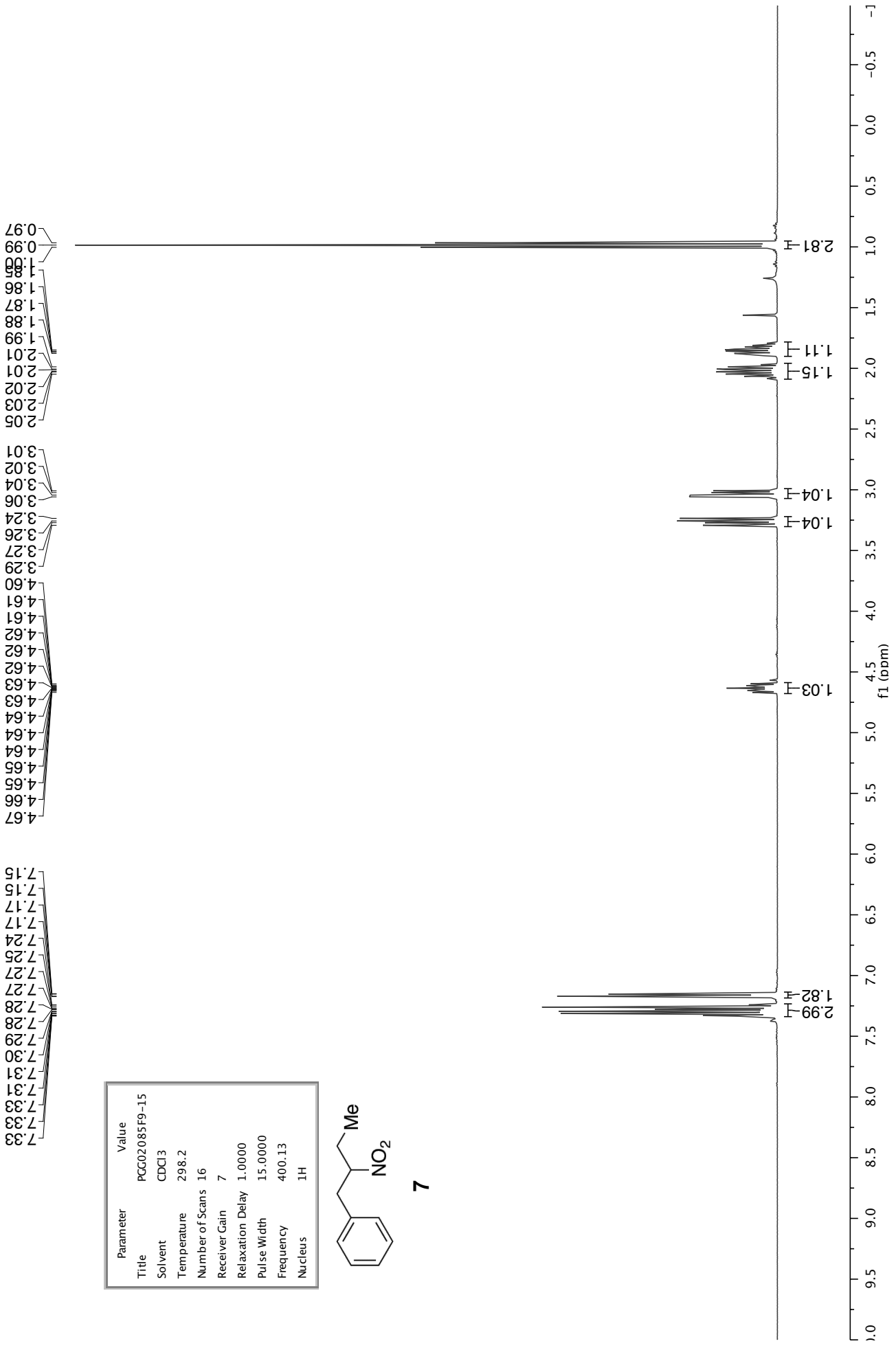
(11) Gilbert, K. E.; Borden, W. T. *J. Org. Chem.* **1979**, *44*, 659.

(12) Ballini, R.; Bosica, G. *Eur. J. Org. Chem.* **1998**, *1998*, 355.

(13) Patt, S. L.; Shoolery, J. N. *J. Magn. Reson.* **1982**, *46*, 535.

(14) Tang, L.-M.; Duan, Y.-Q.; Li, X.-F.; Li, Y.-S. *J. Organomet. Chem.* **2006**, *691*, 2023.

(15) Badiei, Y. M.; Dinescu, A.; Dai, X.; Palomino, R. M.; Heinemann, F. W.; Cundari, T. R.; Warren, T. H. *Angew. Chem. Int. Ed.* **2008**, *47*, 9961.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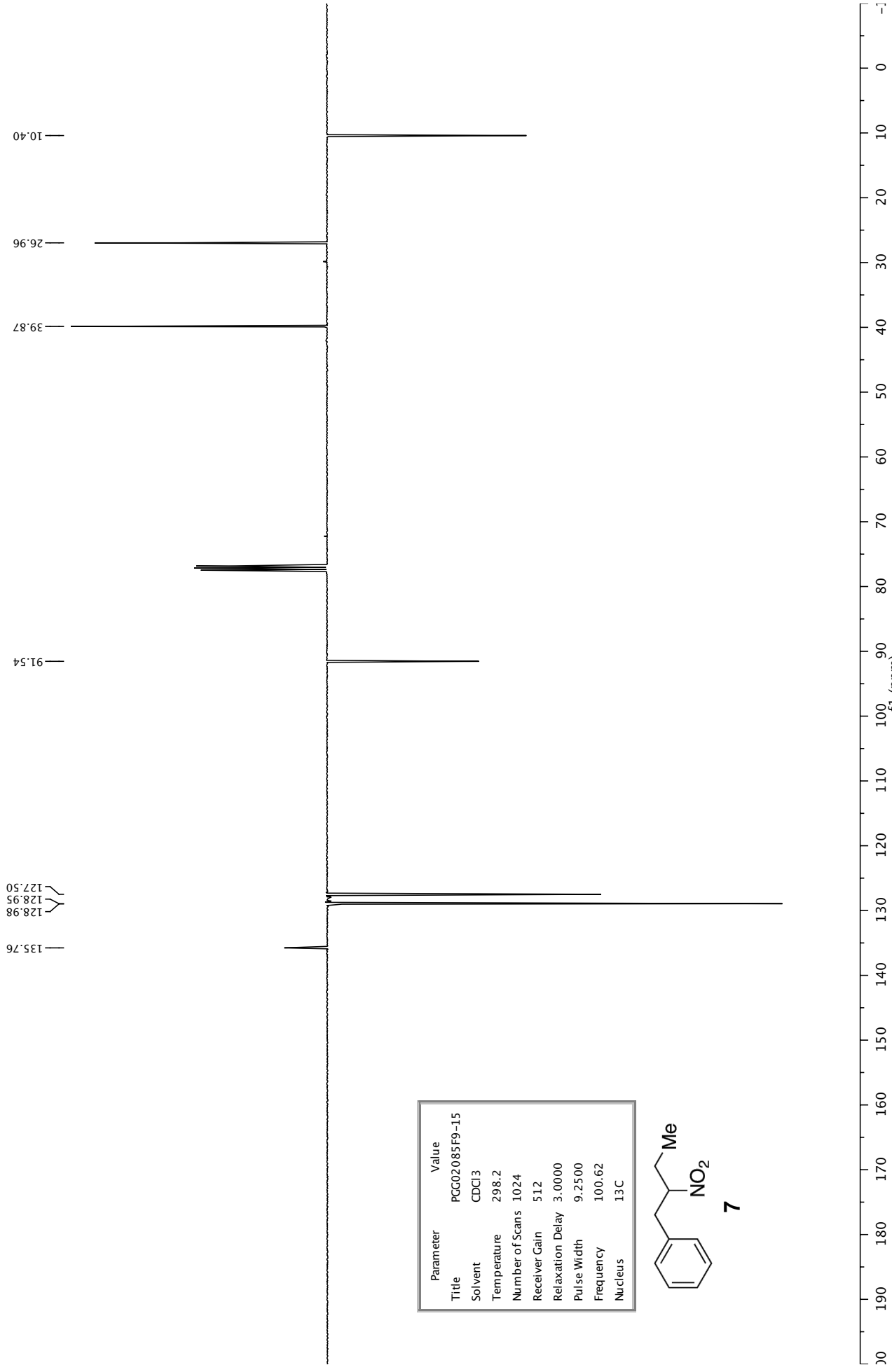
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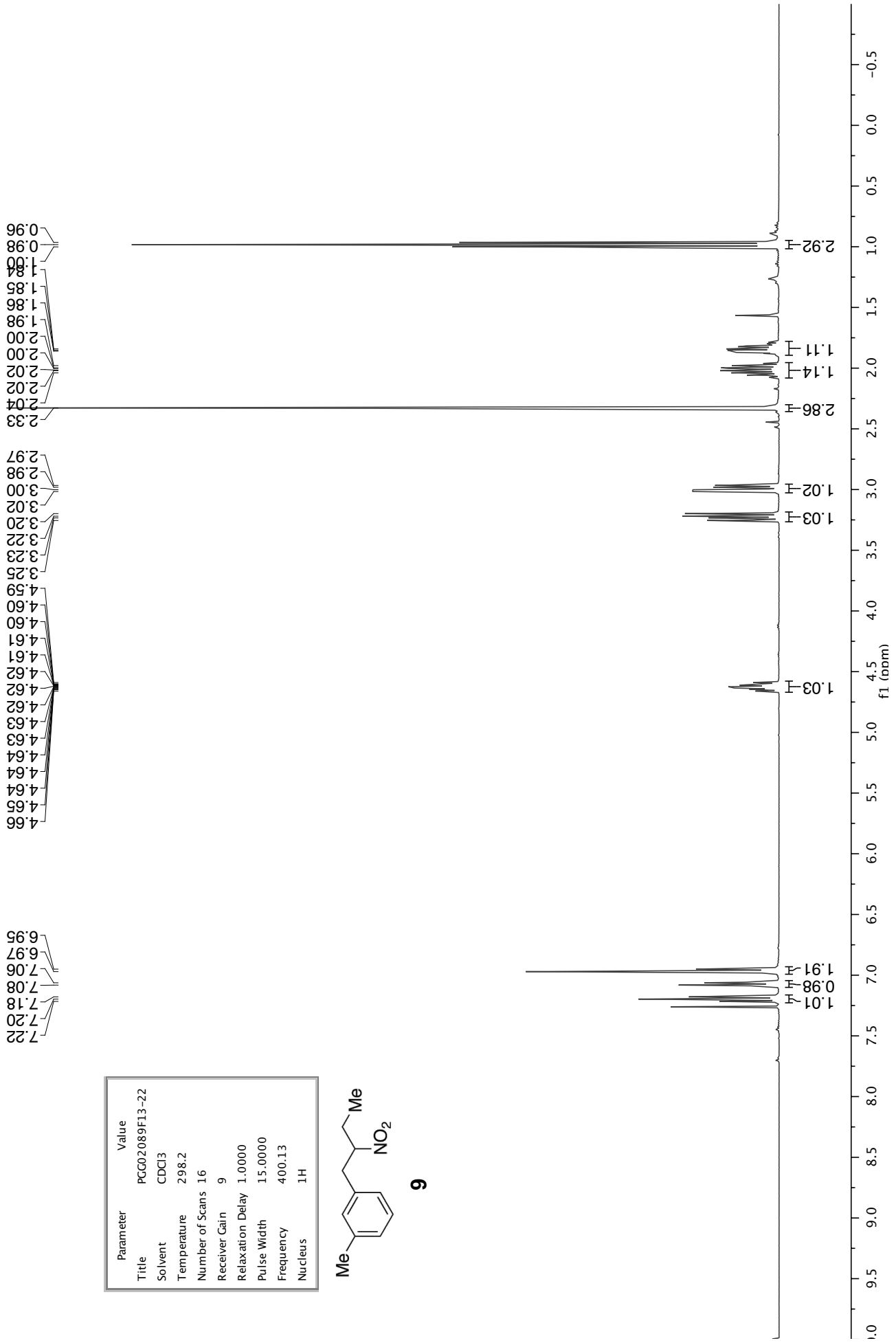
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NO2
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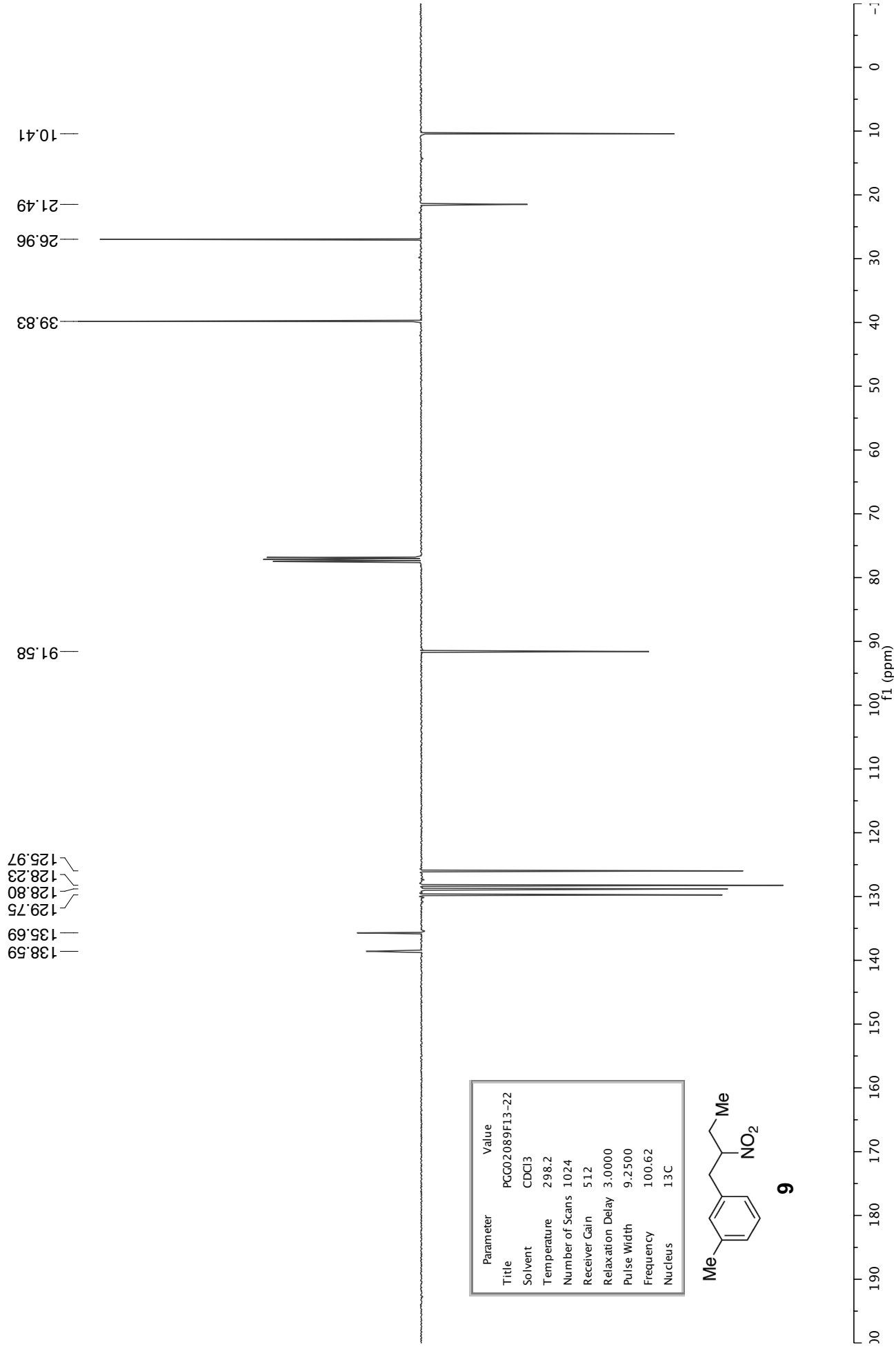
f1 (ppm)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Frequency 100.62
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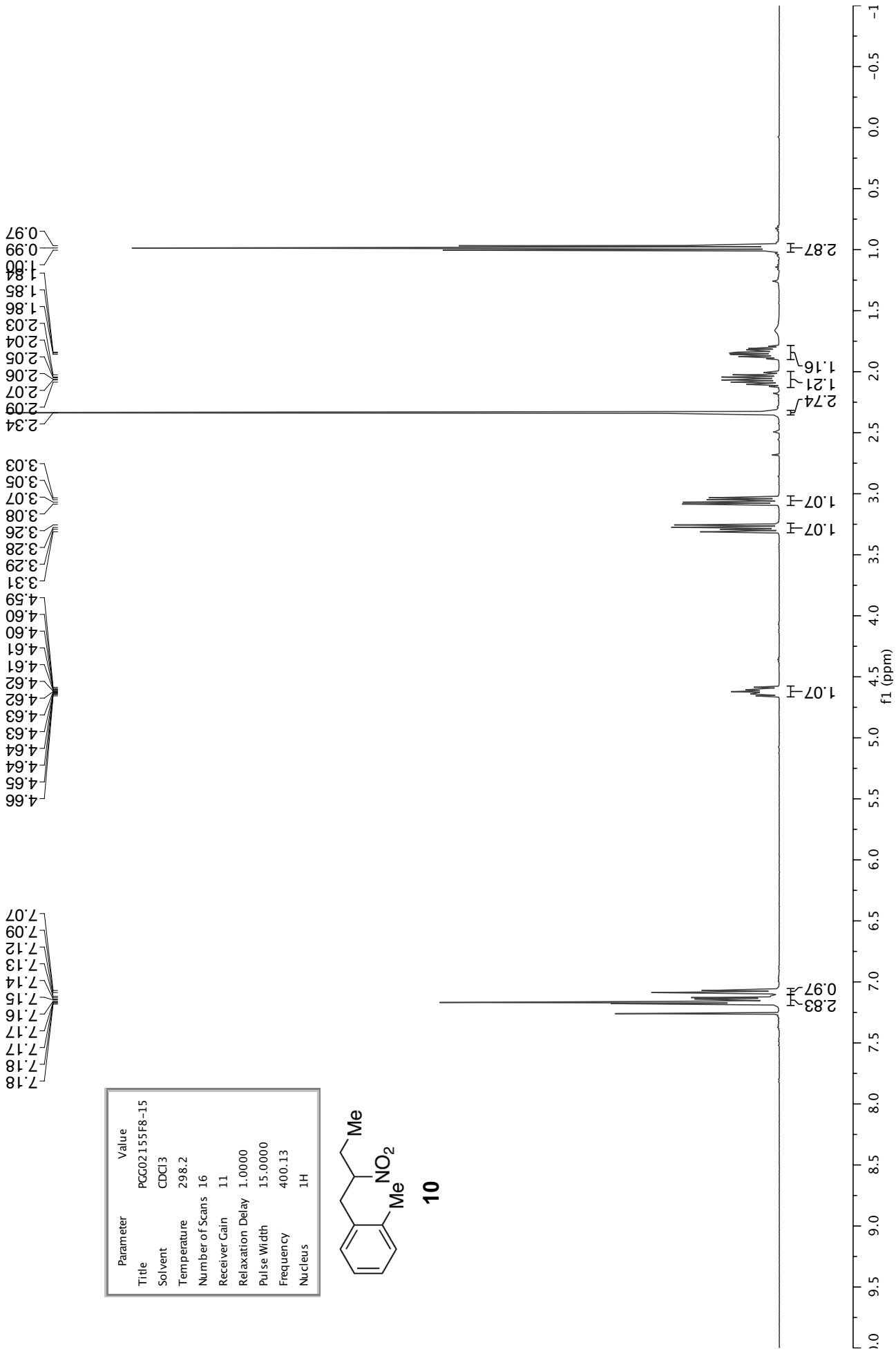
NO2
Me

9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Nucleus 1H
Me
NO2
Me
10
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4.66 4.65 4.64 4.64 4.63 4.63 4.62 4.62 4.61 4.61 4.60 4.60 4.59
3.31 3.29 3.28 3.26 3.08 3.07 3.05 3.03
2.34 2.09 2.07 2.06 2.05 2.04 2.03 1.86 1.85 1.84 1.00 0.99 0.97
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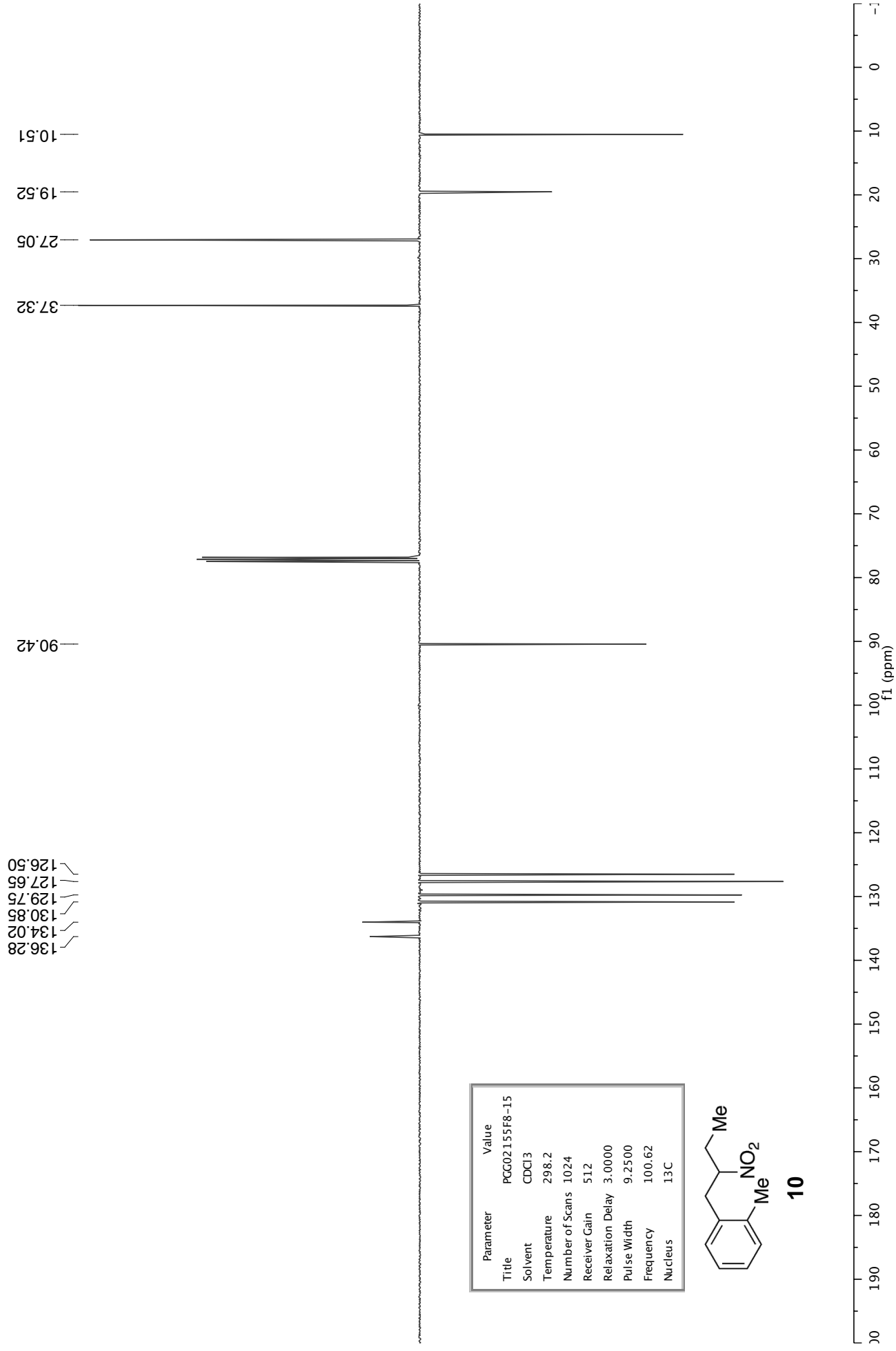
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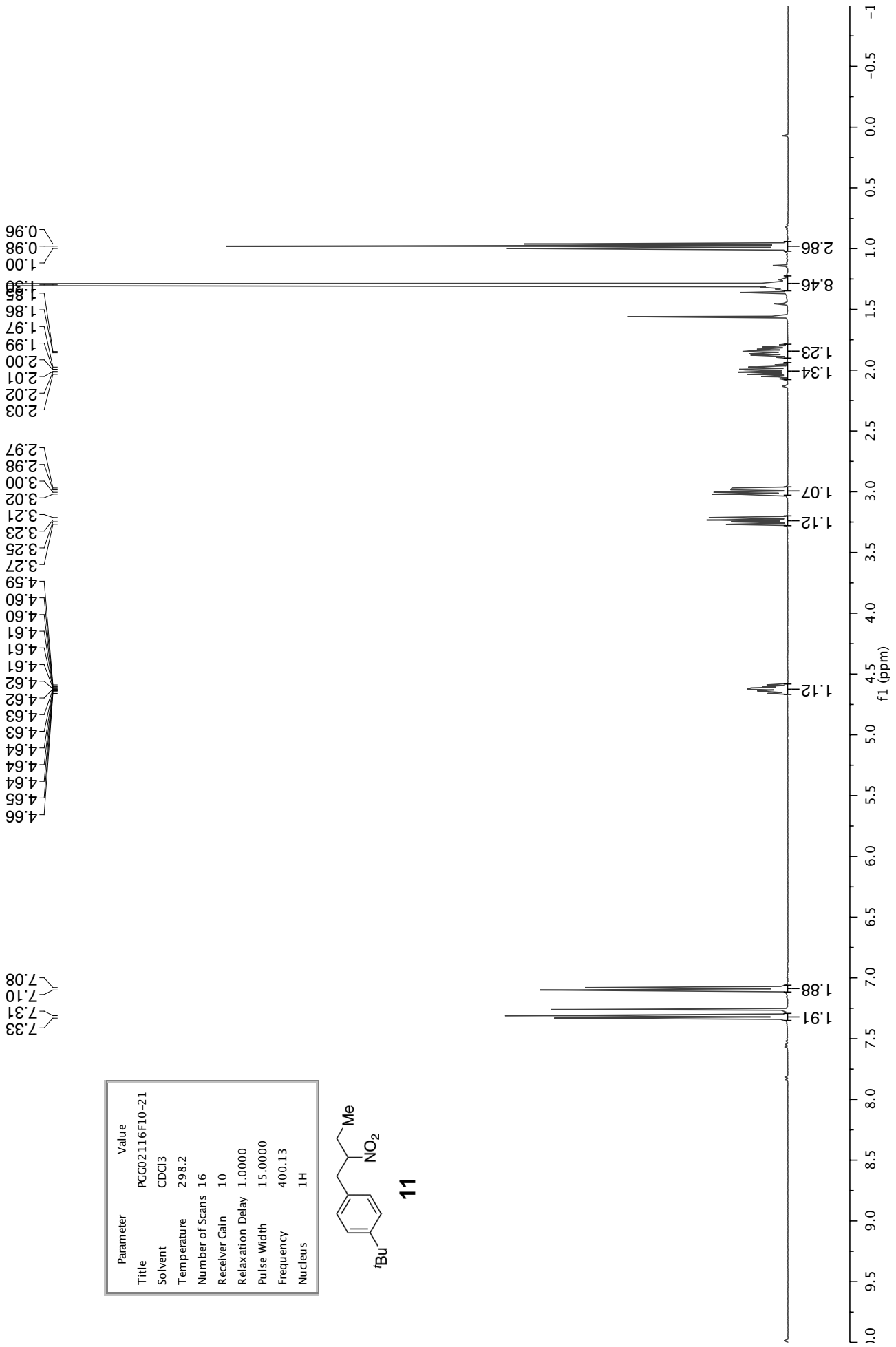
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tBu
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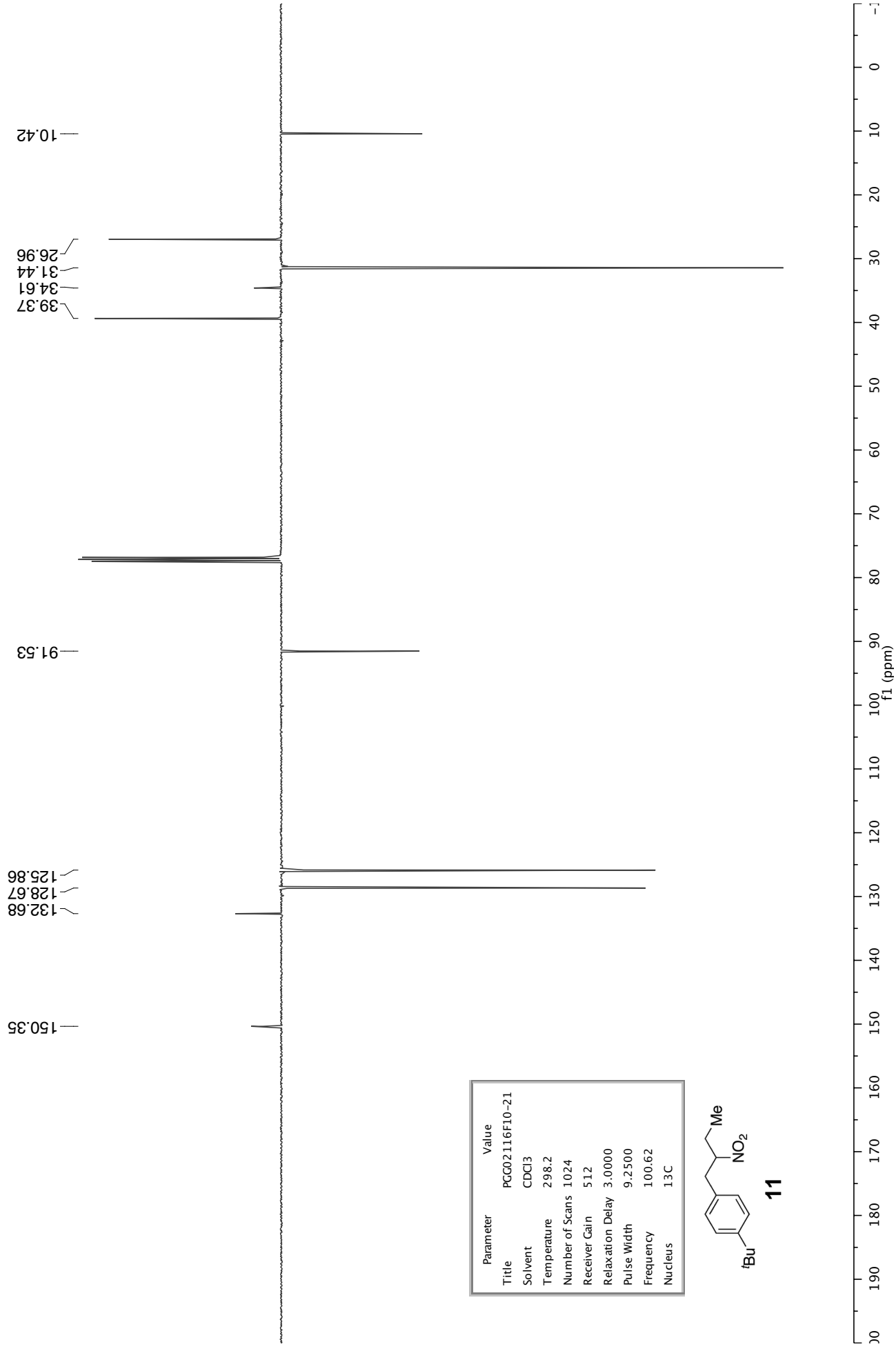
f1 (ppm)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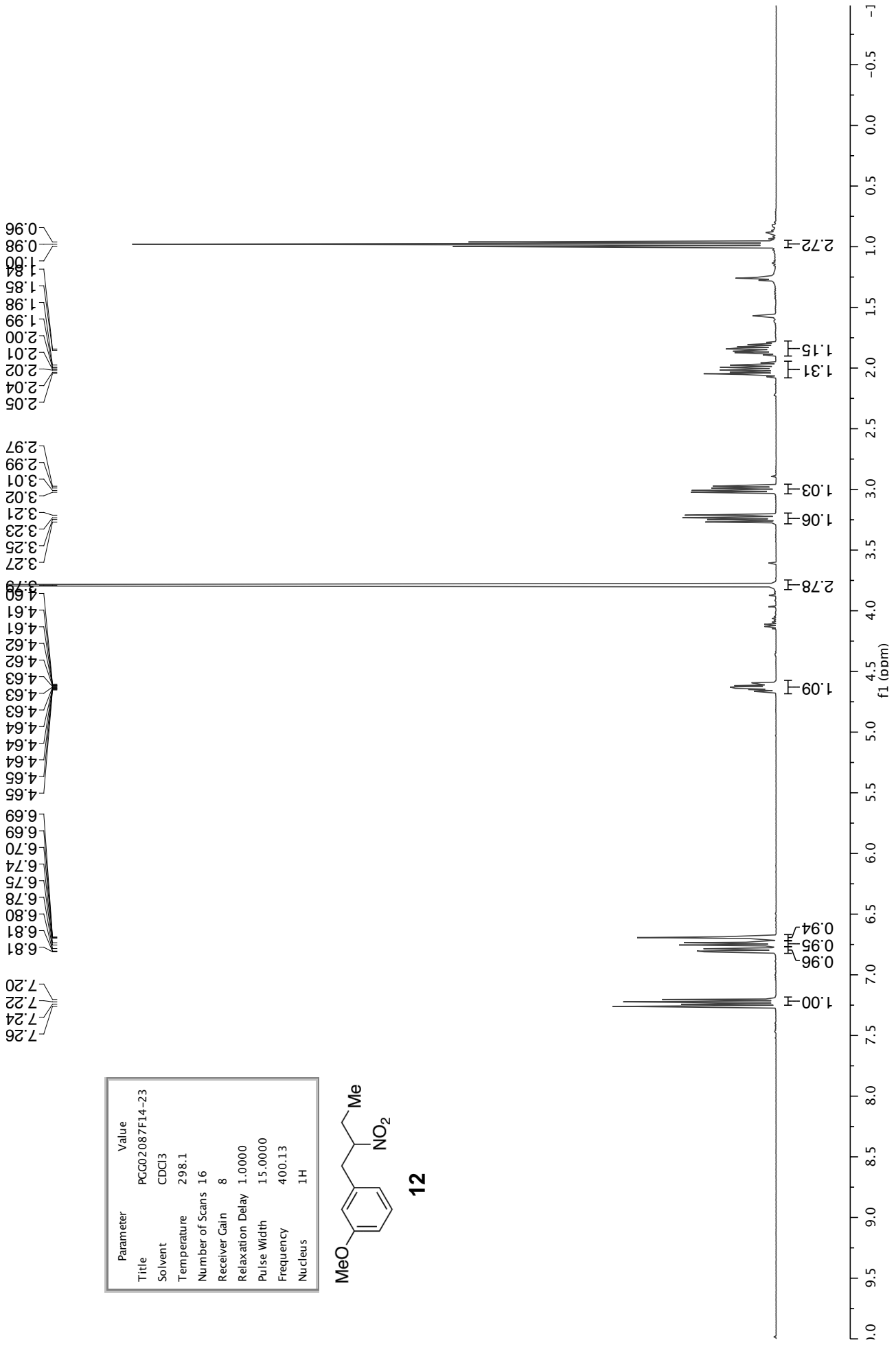
NO2
tBu

11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Me
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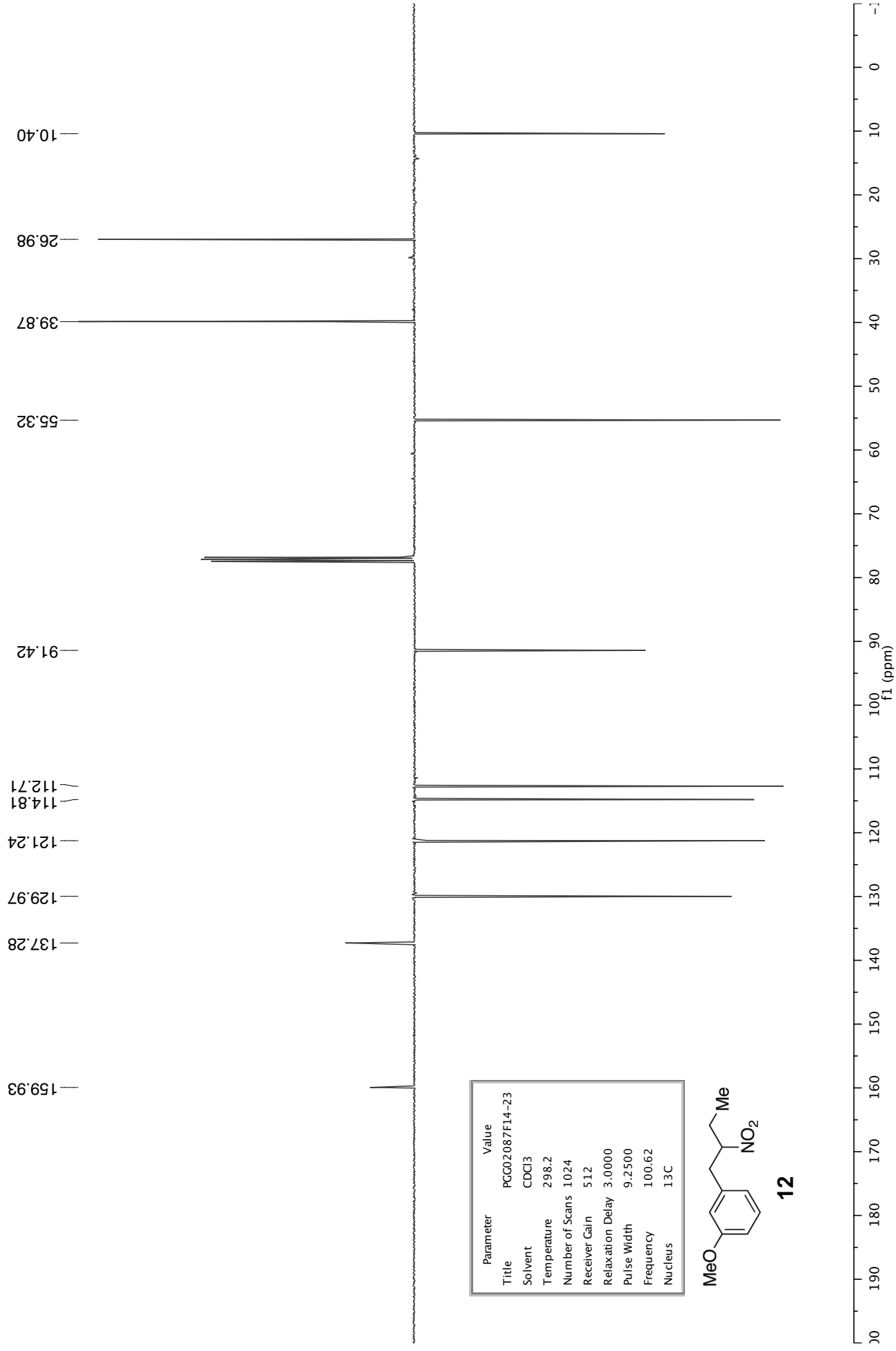
f1 (ppm)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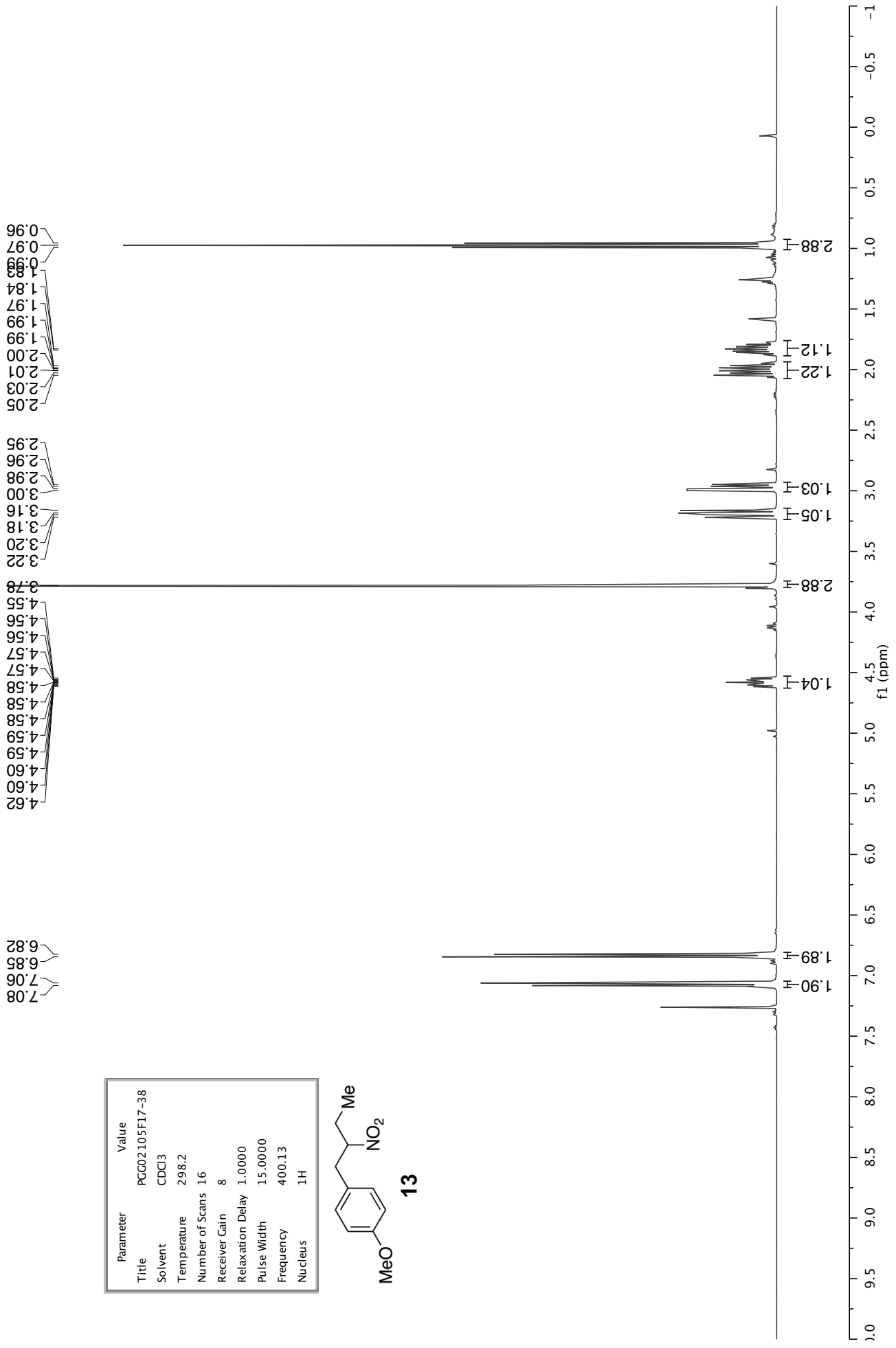
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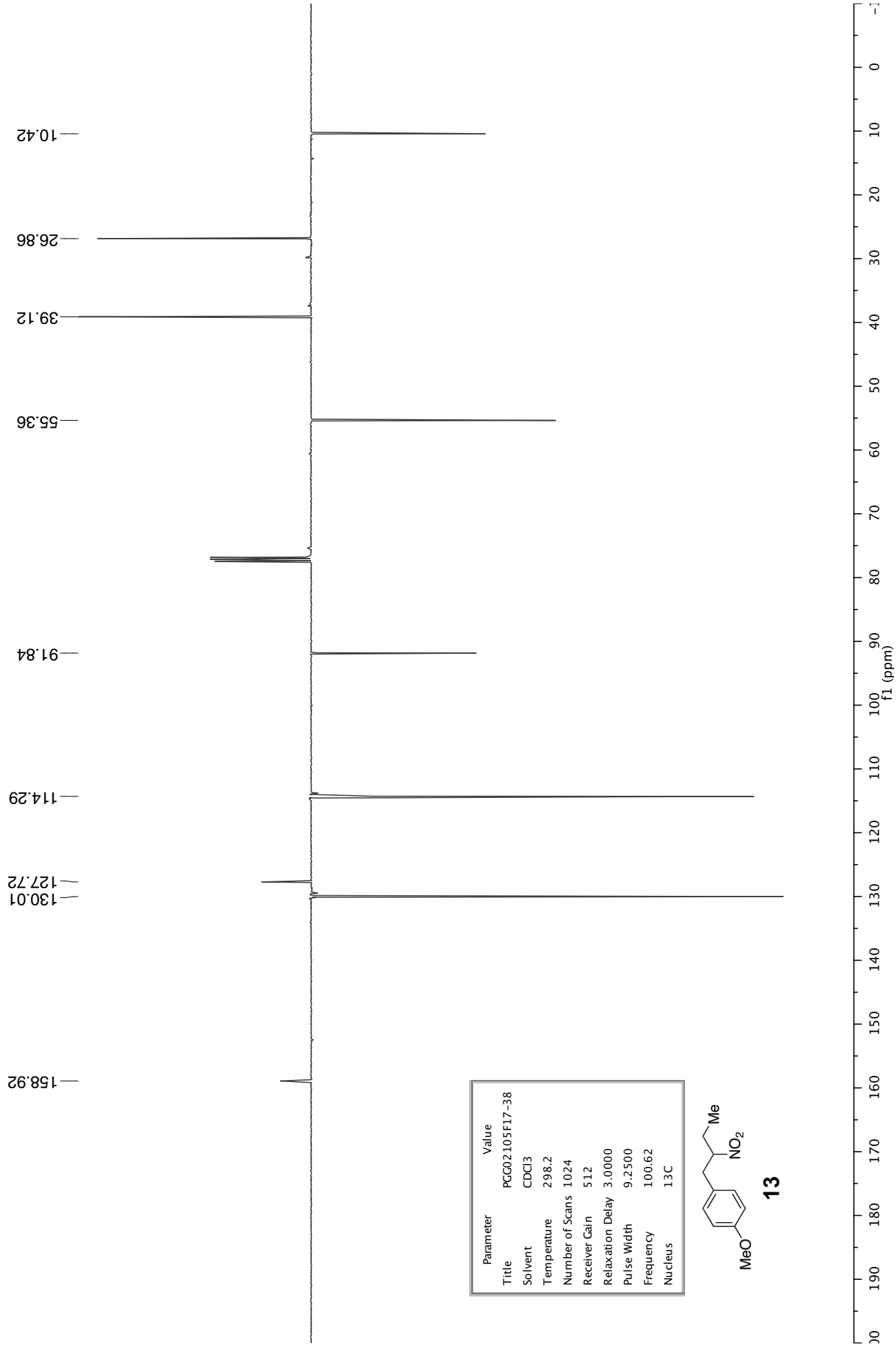
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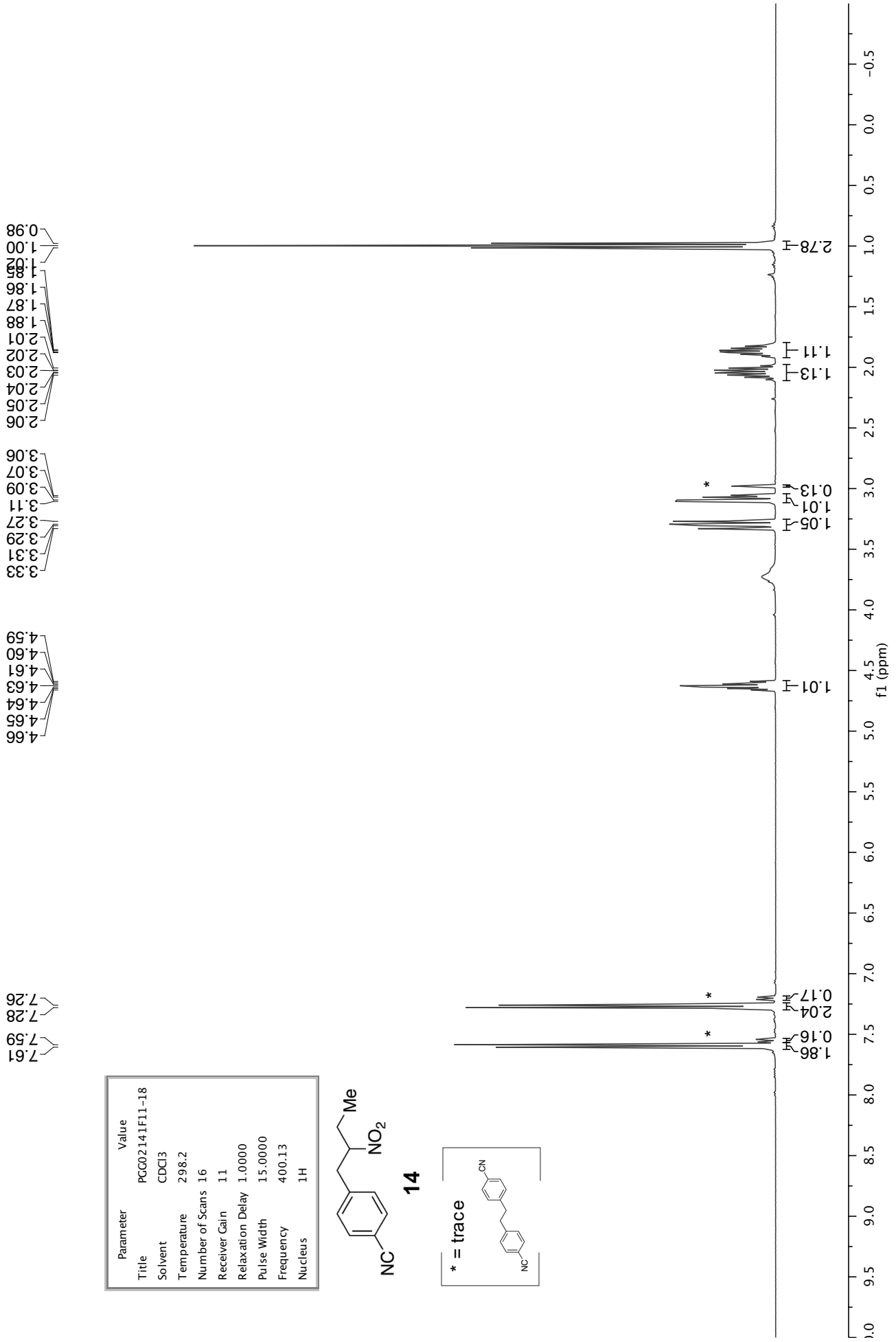
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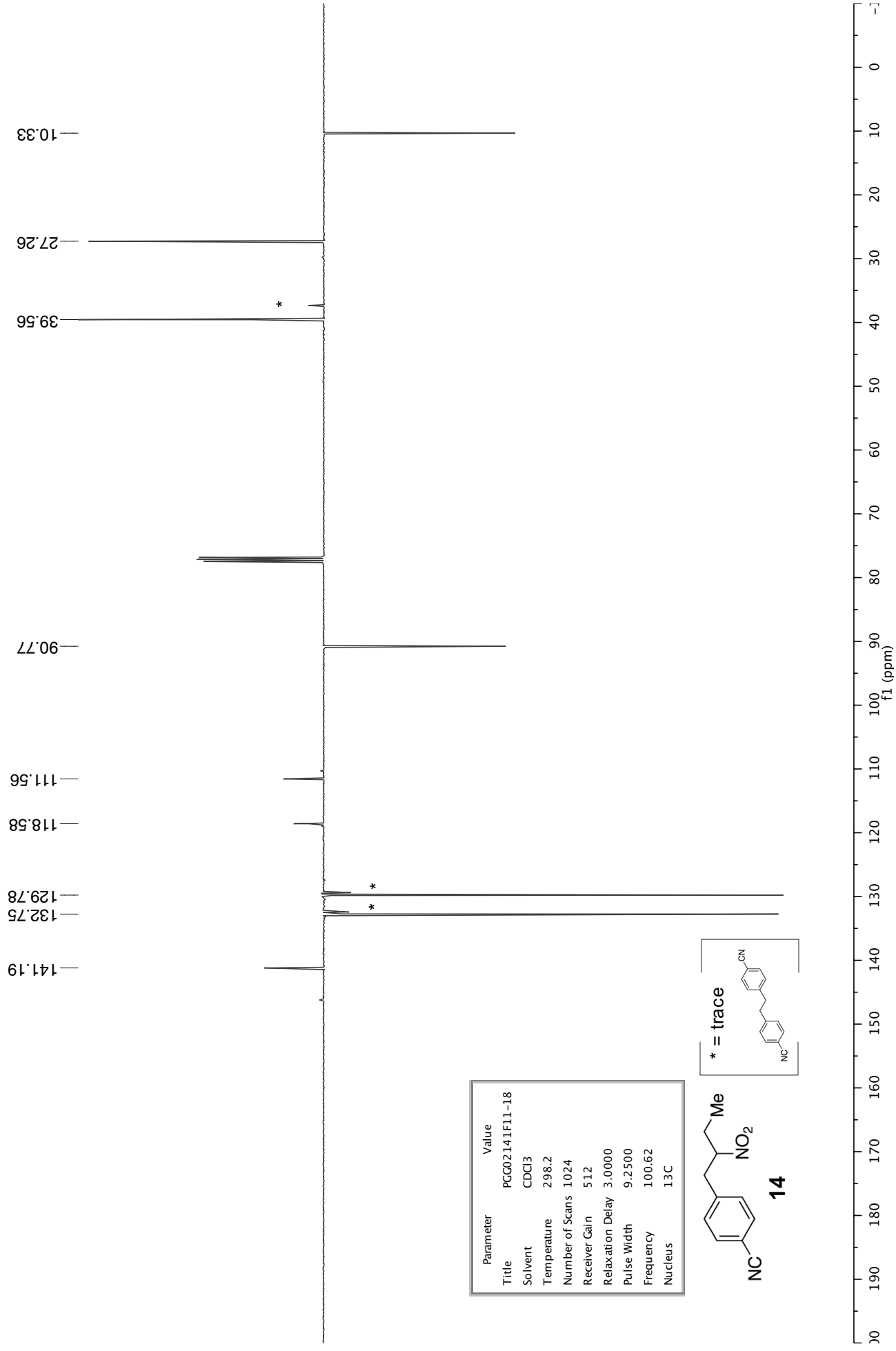
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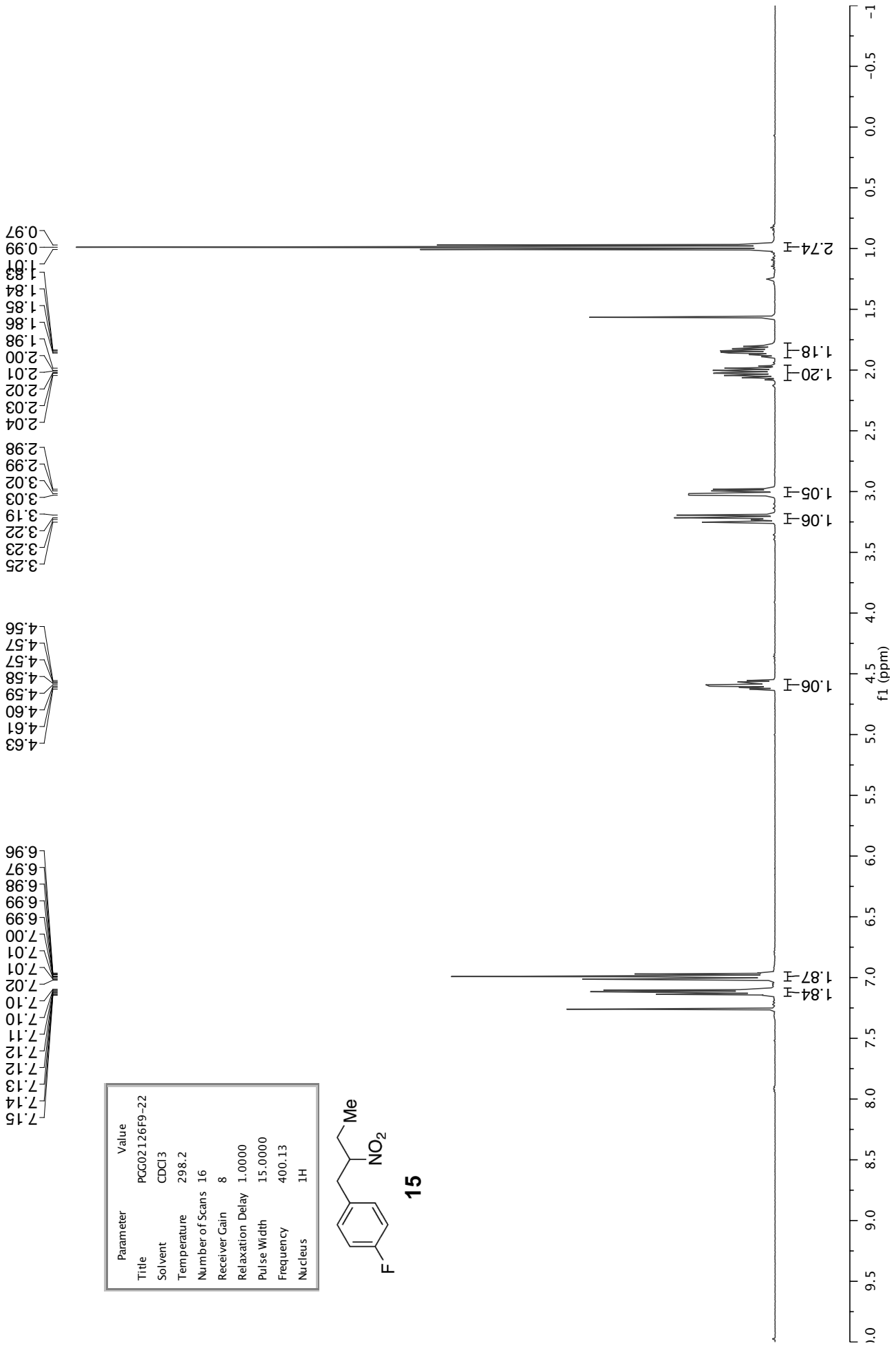
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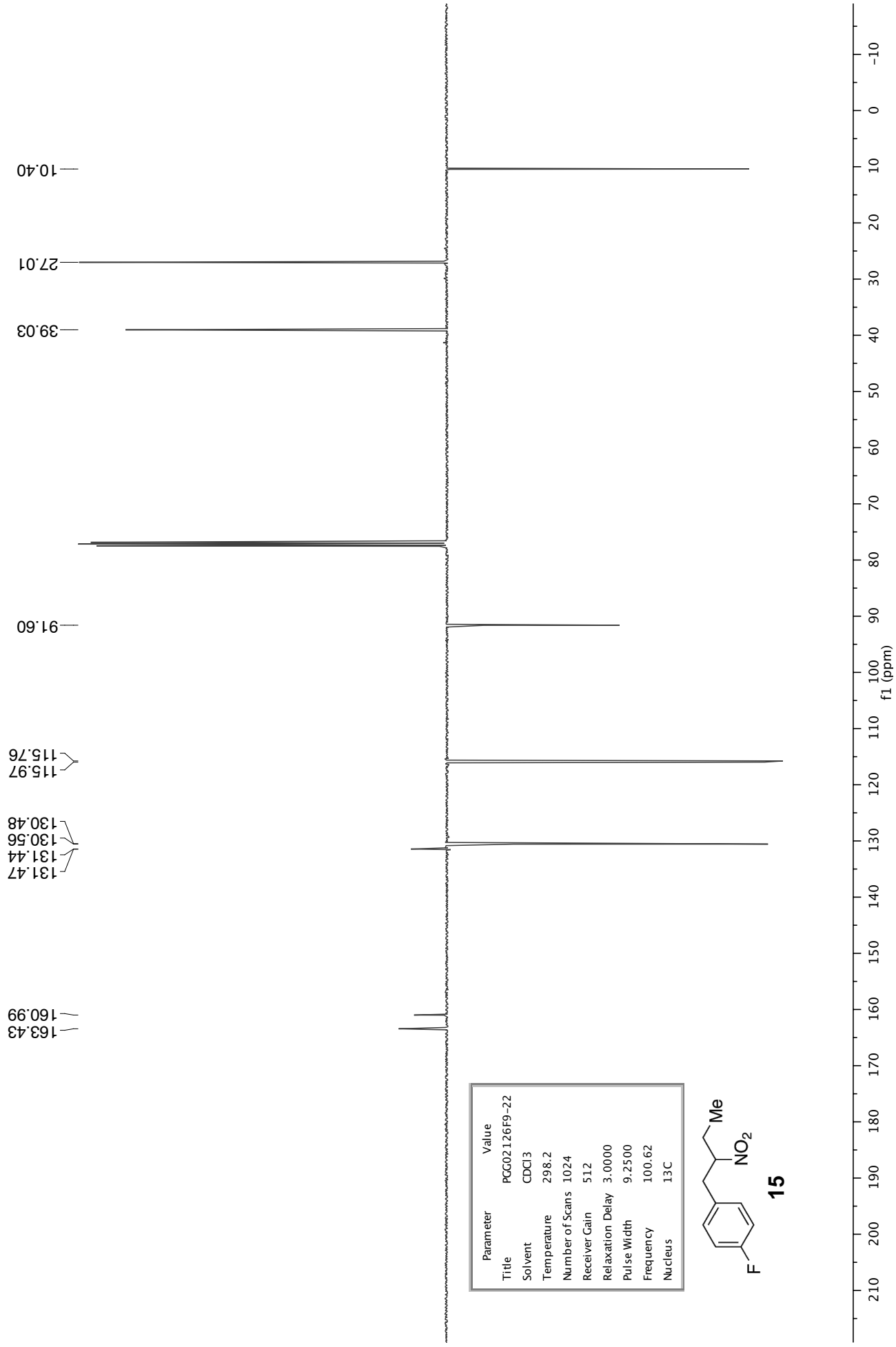
15
f1 (ppm)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Frequency 100.62
Nucleus 13C
Me
NO2
F
15

Parameter	Value
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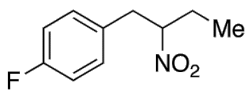

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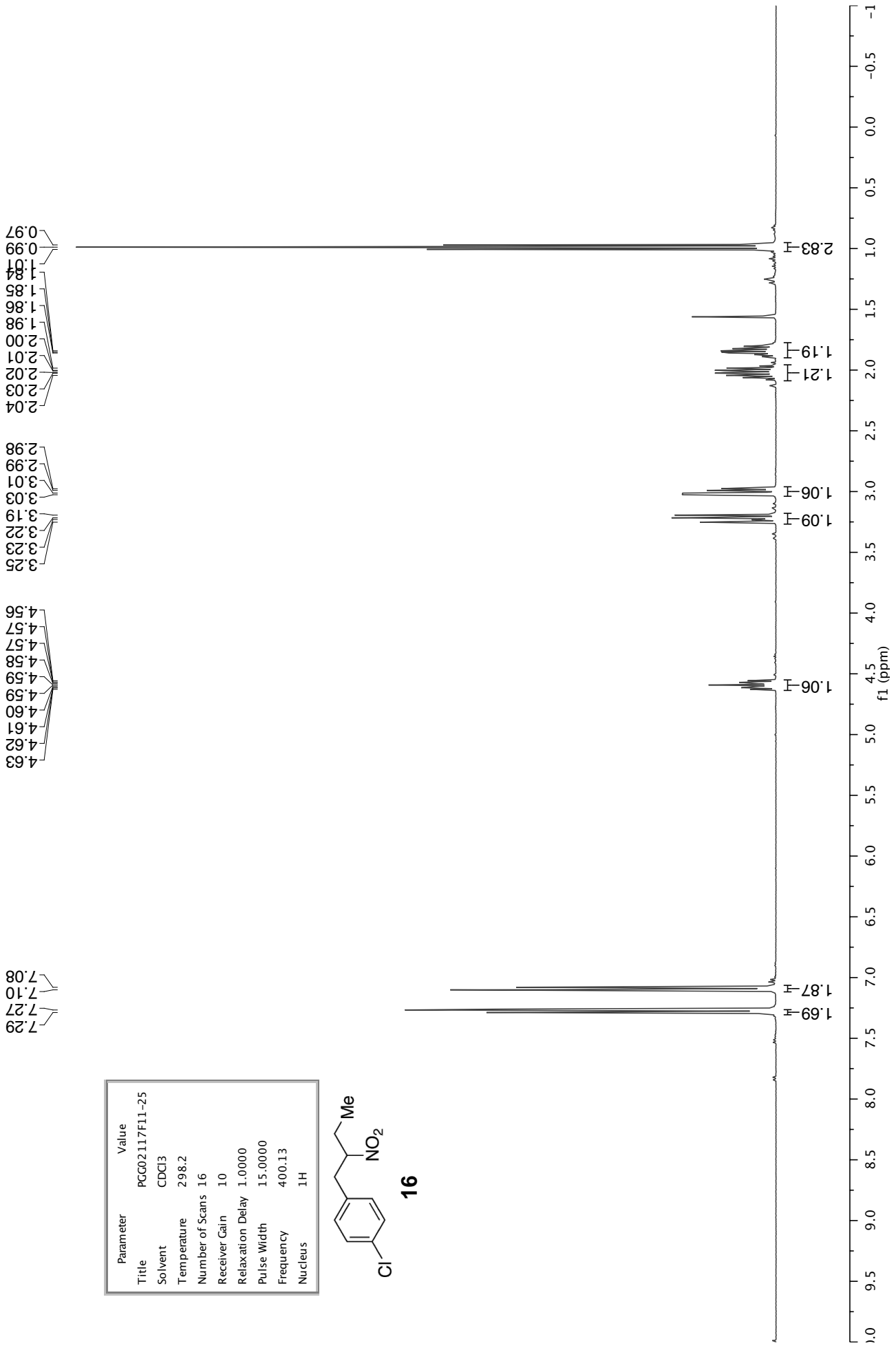
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NO2
Cl
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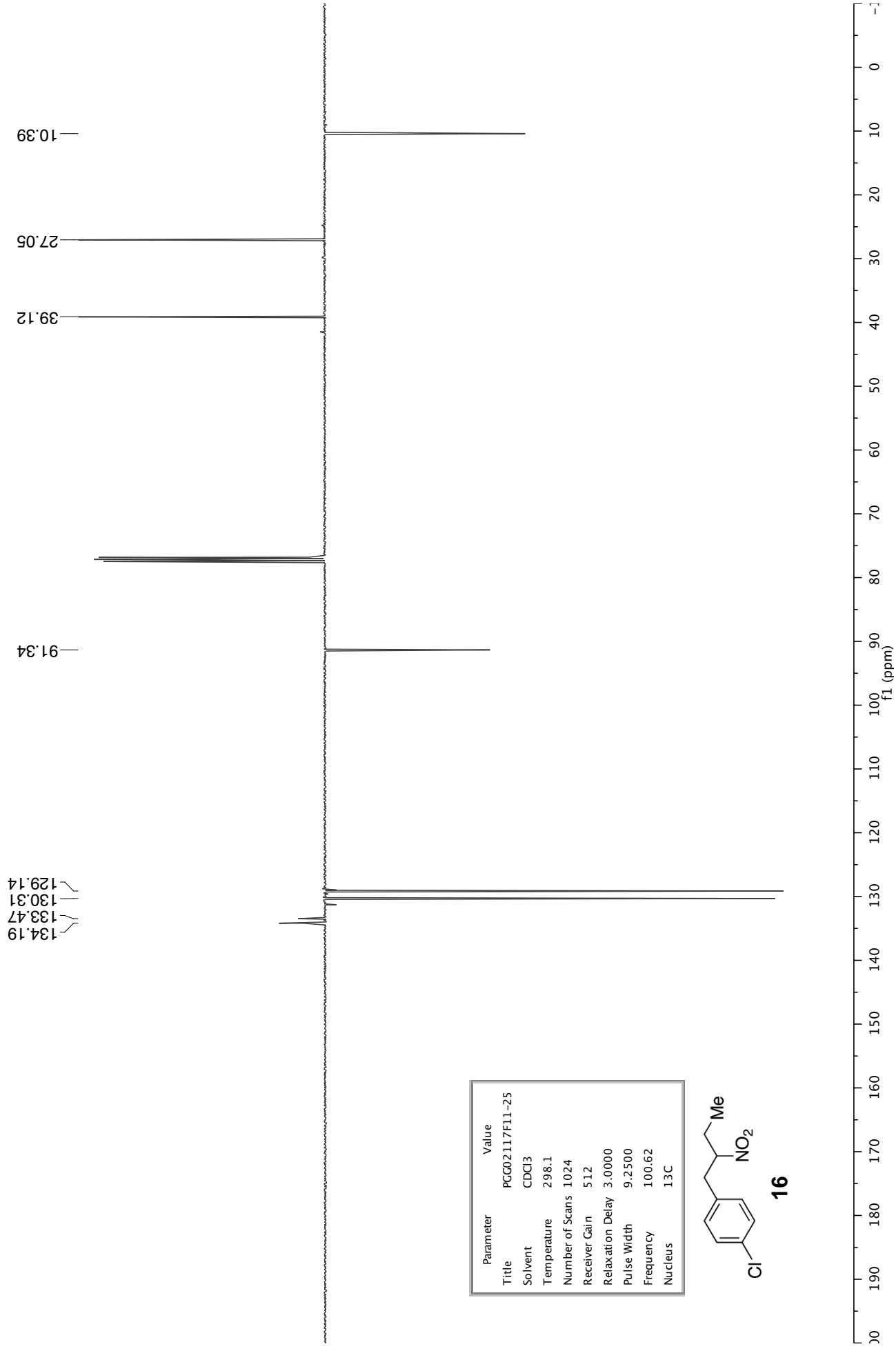
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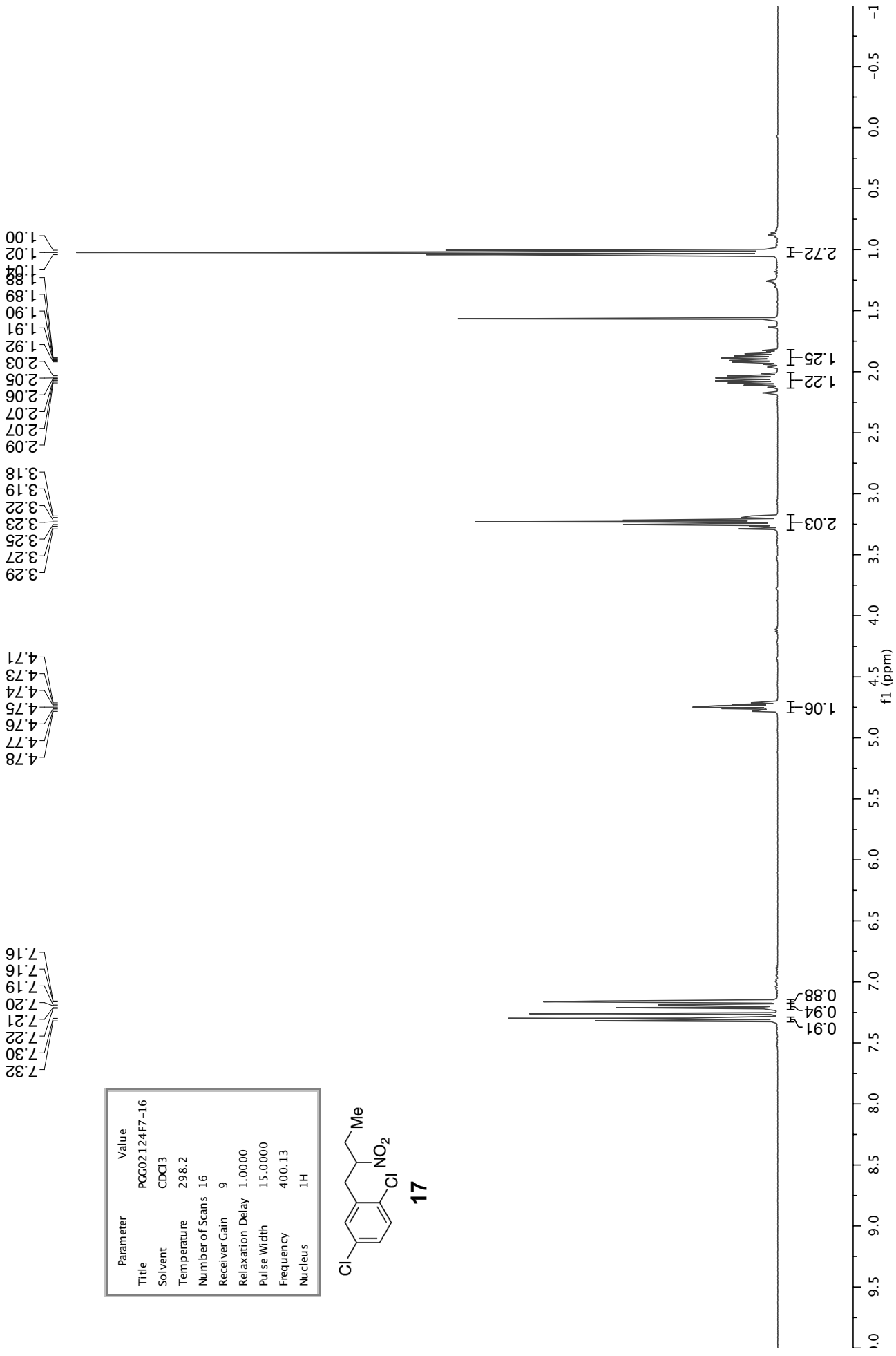
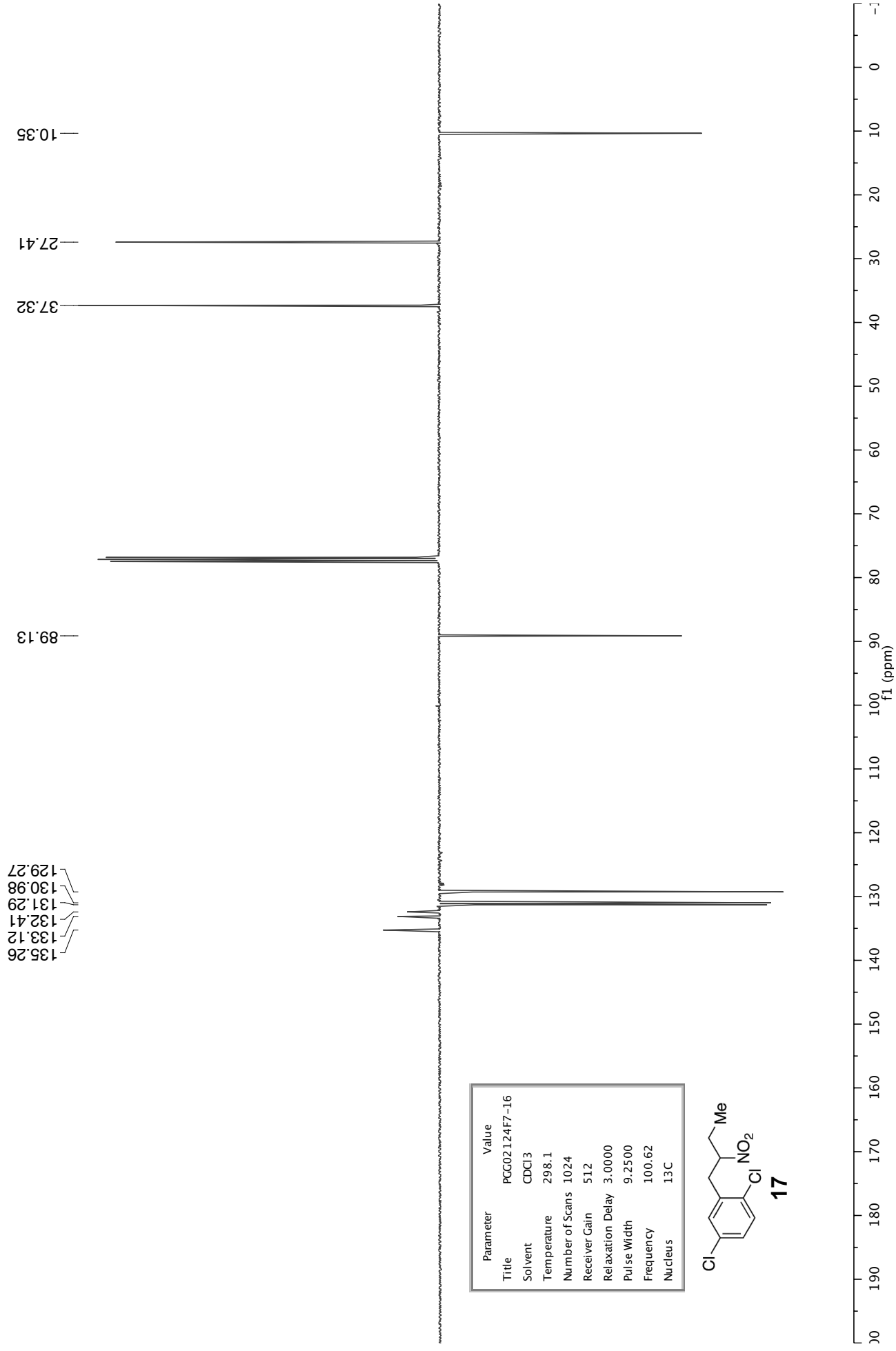
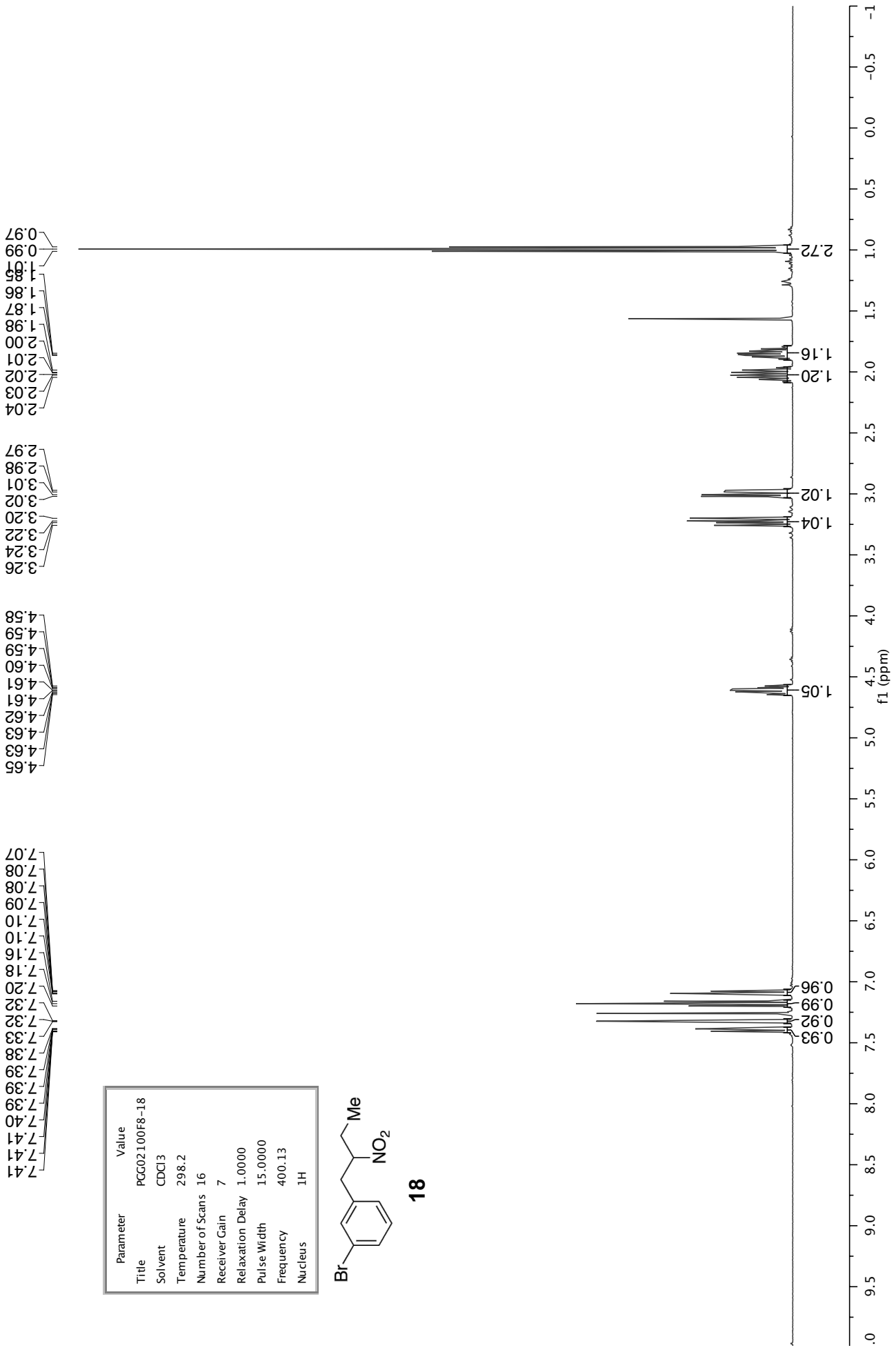
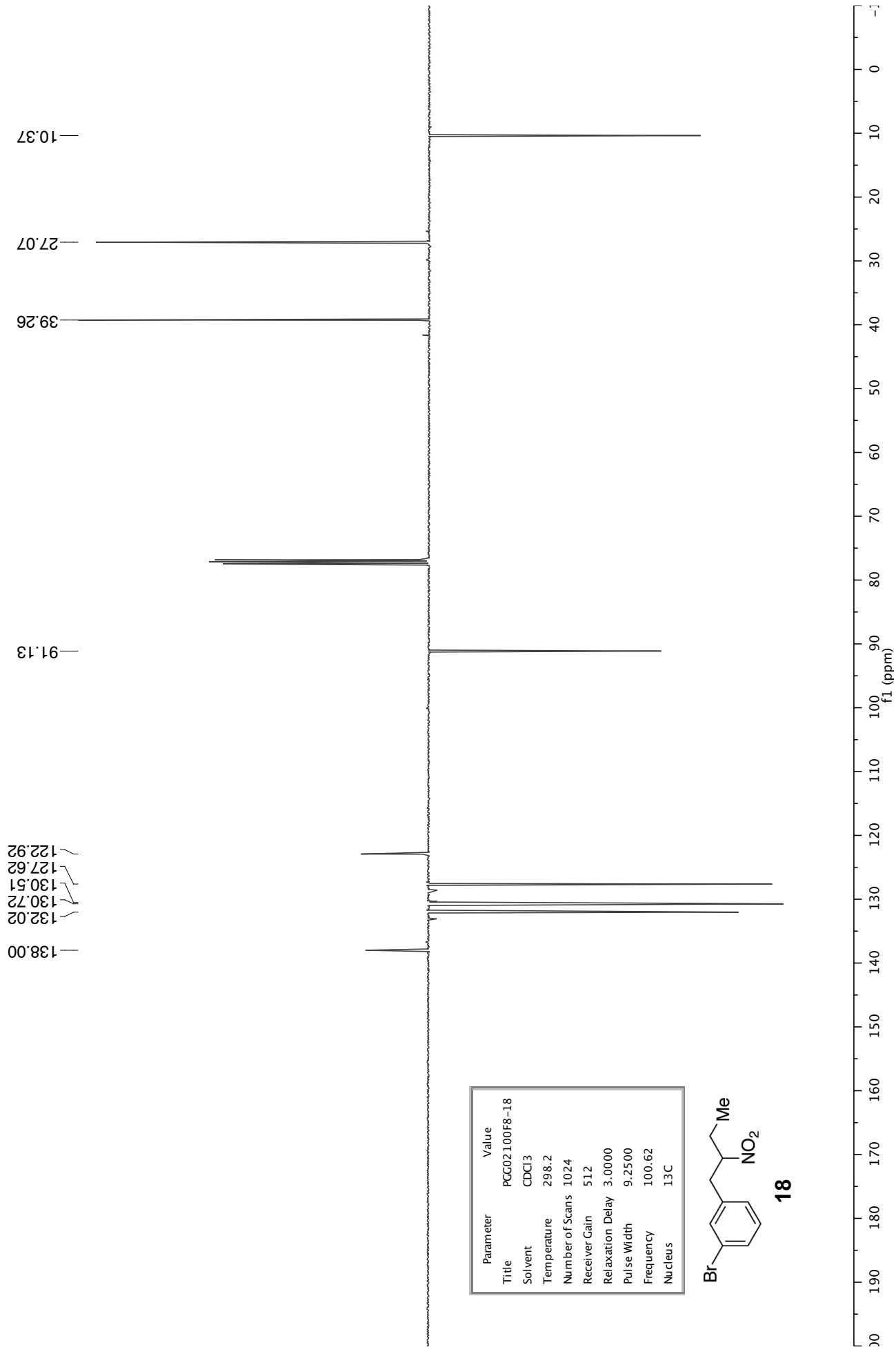
Cl

16

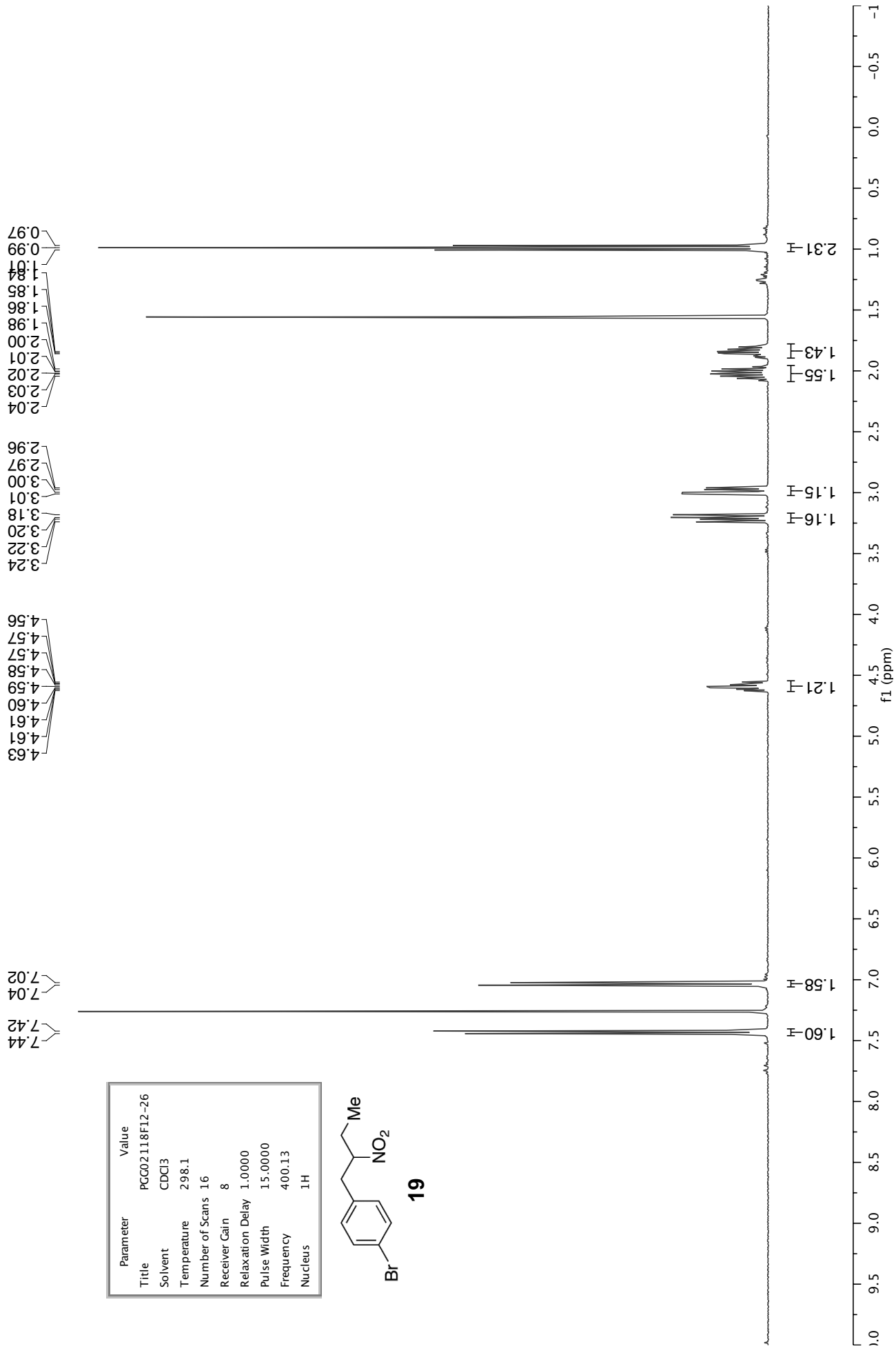

Parameter Value
Title PGG02124F7-16
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 9
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
Me
NO2
Cl
Cl
17
7.32
7.30
7.22
7.21
7.20
7.19
7.16
7.16
4.78
4.77
4.76
4.75
4.74
4.73
4.71
3.29
3.27
3.25
3.23
3.22
3.19
3.18
2.09
2.07
2.07
2.06
2.05
2.03
1.92
1.91
1.90
1.89
1.88
1.04
1.02
1.00
0.91
0.94
0.88
2.72
1.25
1.22
2.03
1.06
f1 (ppm)

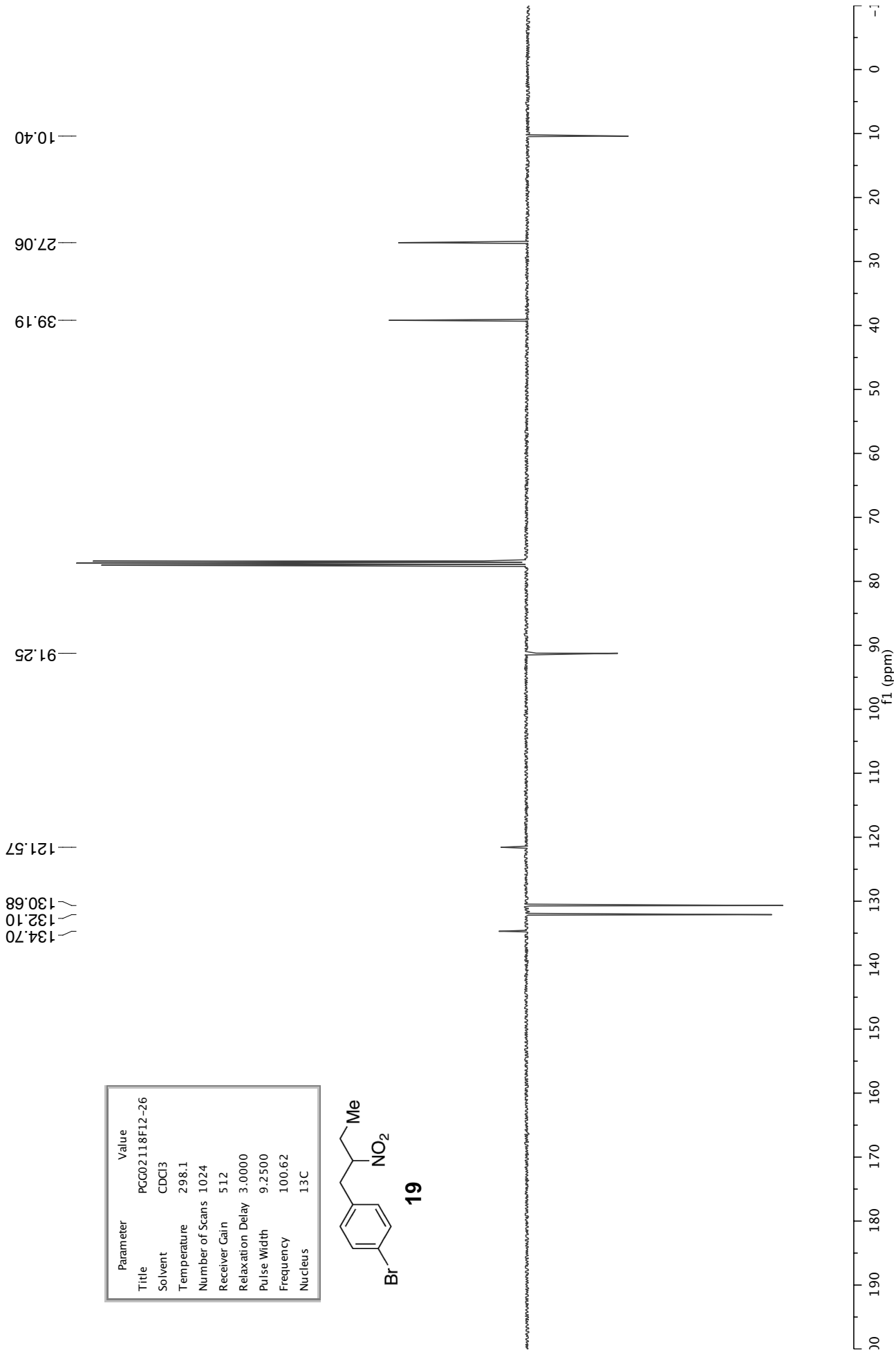

10.35
27.41
37.32
89.13
129.27
130.98
131.29
132.41
133.12
135.26
f1 (ppm)
Parameter Value
Title PGG02124F7-16
Solvent CDCl3
Temperature 298.1
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
Me
NO2
Cl
Cl
17

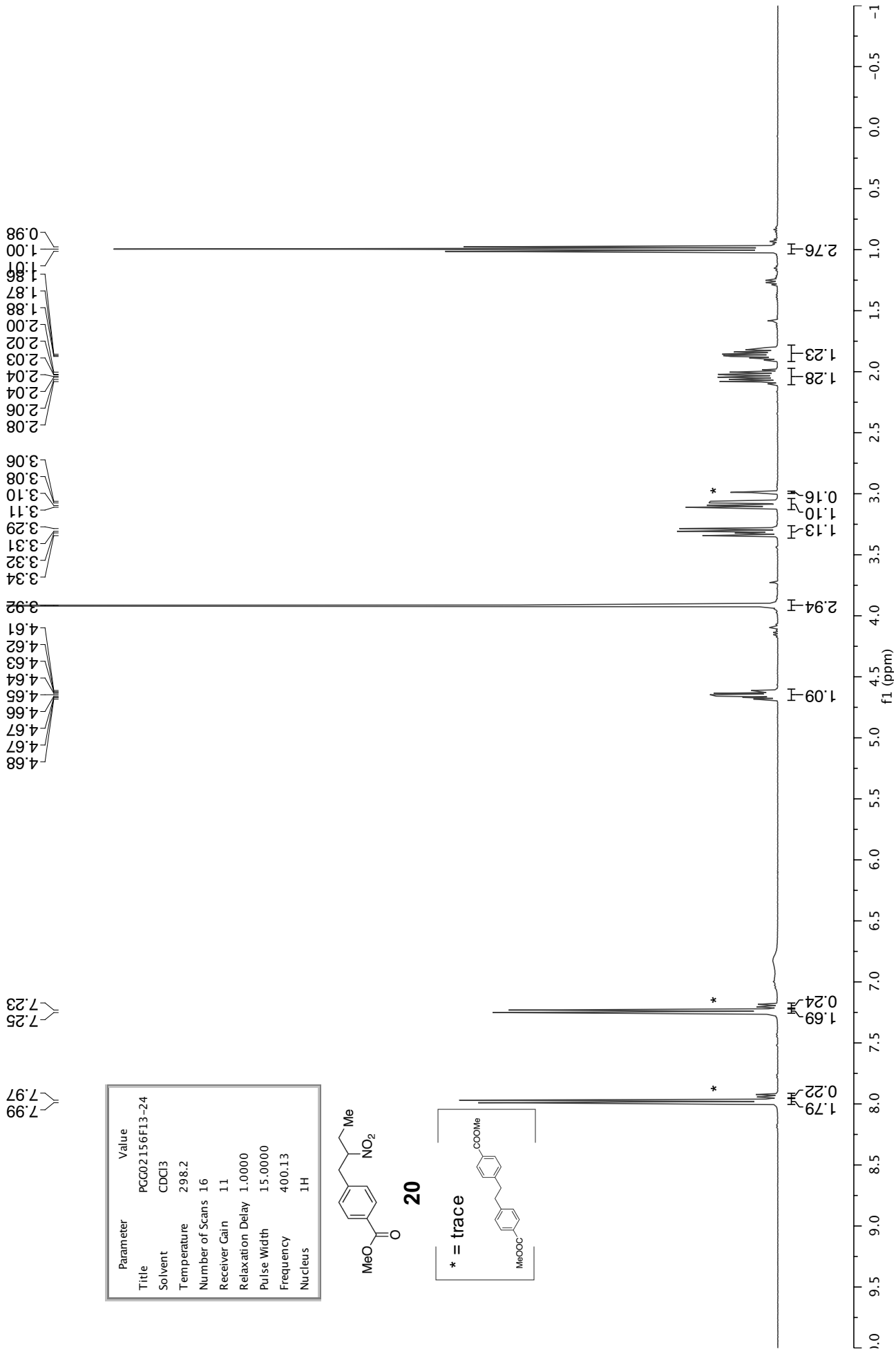

Parameter Value
Title PGG02100F8-18
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 7
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
Br
Me
NO2
18
f1 (ppm)

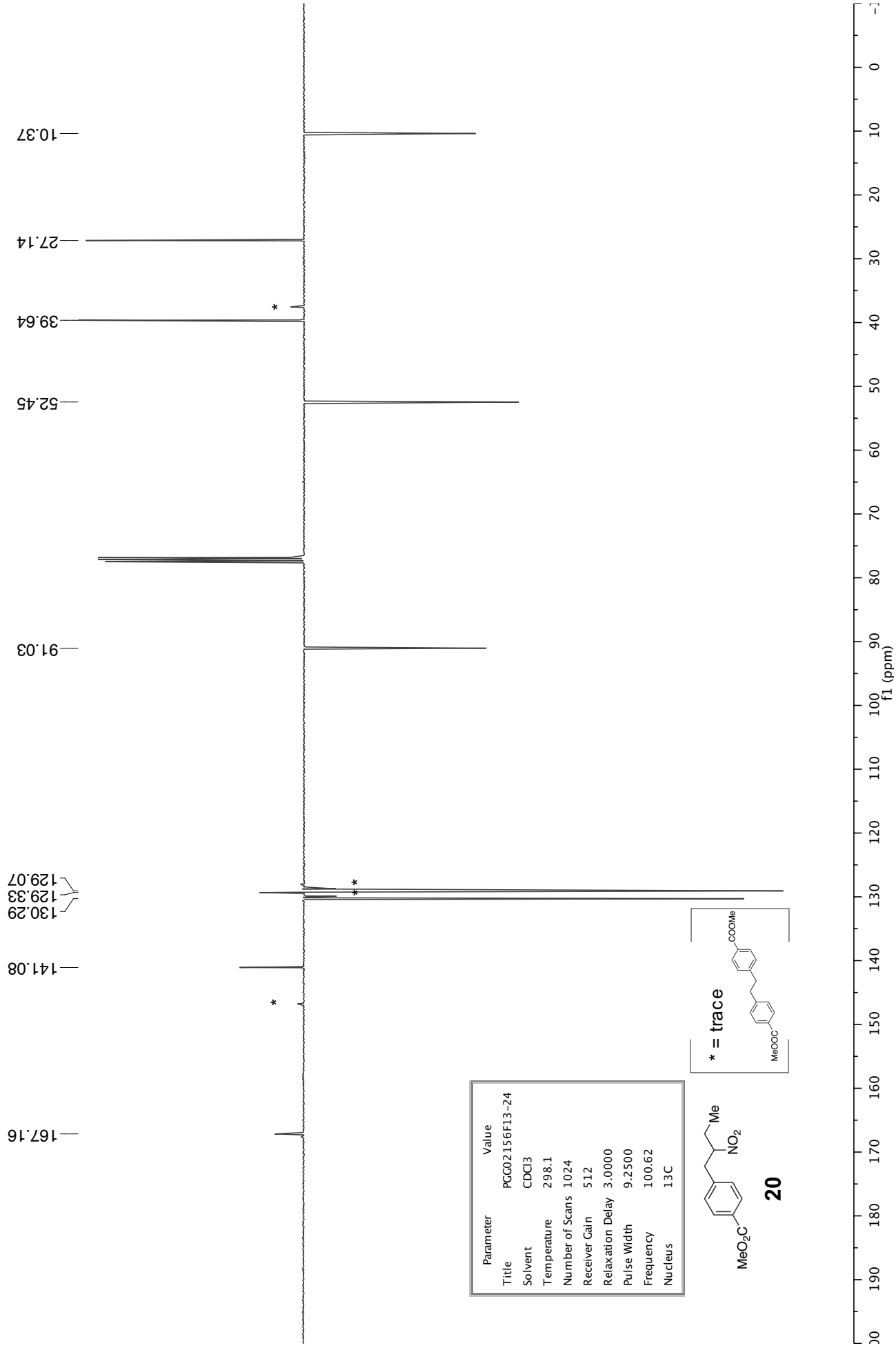

10.37
27.07
39.26
91.13
122.92
127.62
130.51
130.72
132.02
138.00
f1 (ppm)
Parameter Value
Title PGG02100F8-18
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
Br
NO2
Me

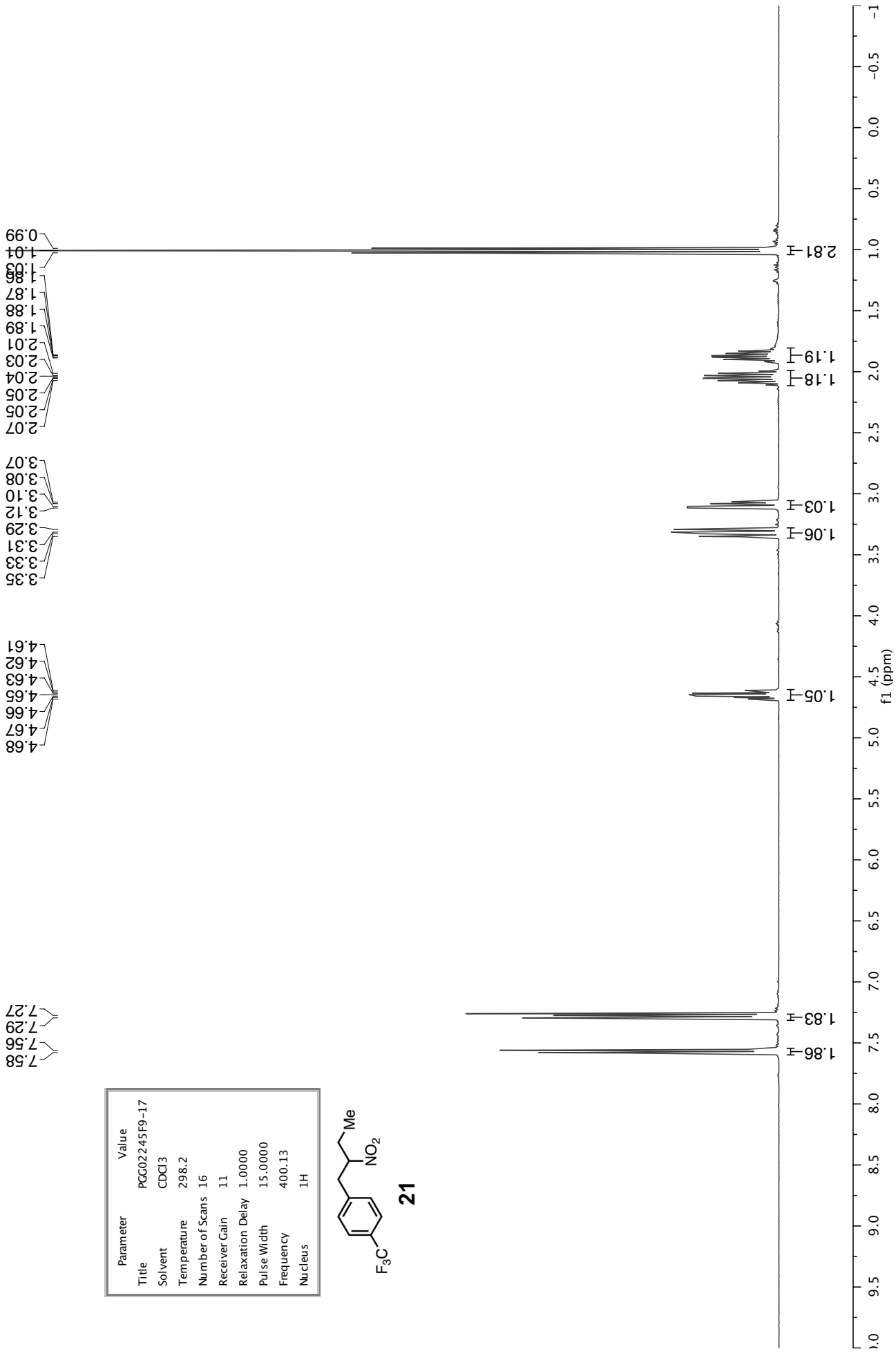
18

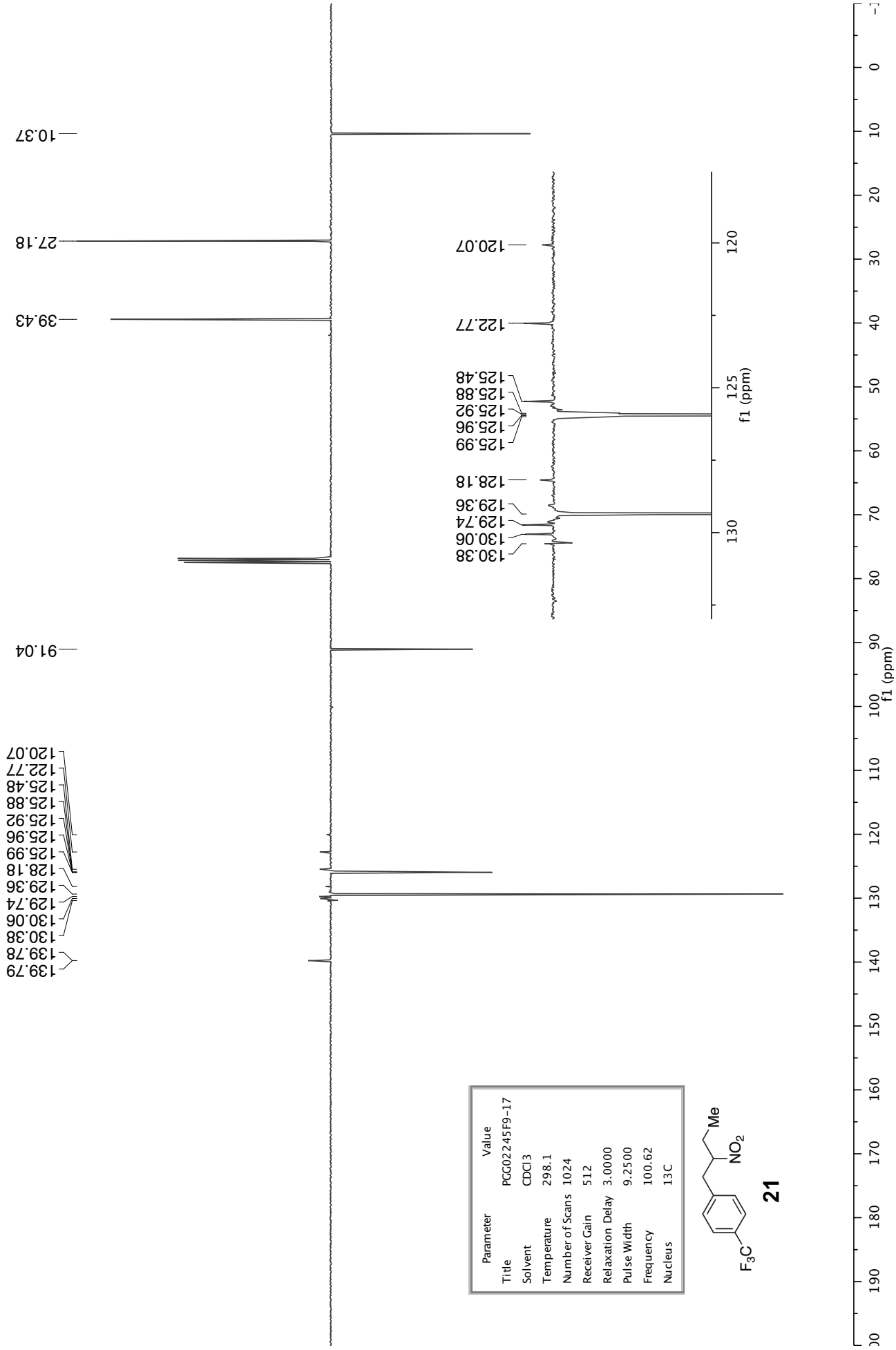

Parameter Value
Title PGG02118F12-26
Solvent CDCl3
Temperature 298.1
Number of Scans 16
Receiver Gain 8
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
Br
NO2
Me
19
7.44
7.42
7.04
7.02
4.63
4.61
4.61
4.60
4.59
4.58
4.57
4.57
4.56
3.24
3.22
3.20
3.18
3.01
3.00
2.97
2.96
2.04
2.03
2.02
2.01
2.00
1.98
1.86
1.85
1.84
1.01
0.99
0.97
1.60
1.58
1.21
1.16
1.15
1.55
1.43
2.31
f1 (ppm)


10.40
27.06
39.19
91.25
121.57
130.68
132.10
134.70
f1 (ppm)
Parameter Value
Title PGG02118F12-26
Solvent CDCl3
Temperature 298.1
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
Me
NO2
Br
19

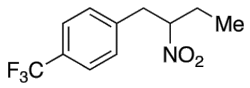

Parameter Value
Title PGG02156F13-24
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 11
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
MeO
O
NO2
Me
20
* = trace
COOMe
MeOOC
f1 (ppm)


10.37
27.14
39.64
52.45
91.03
129.07
129.33
130.29
141.08
167.16
*
f1 (ppm)
Parameter Value
Title PGG02156F13-24
Solvent CDCl3
Temperature 298.1
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
* = trace
COOMe
MeOOC
Me
NO2
MeO2C
20

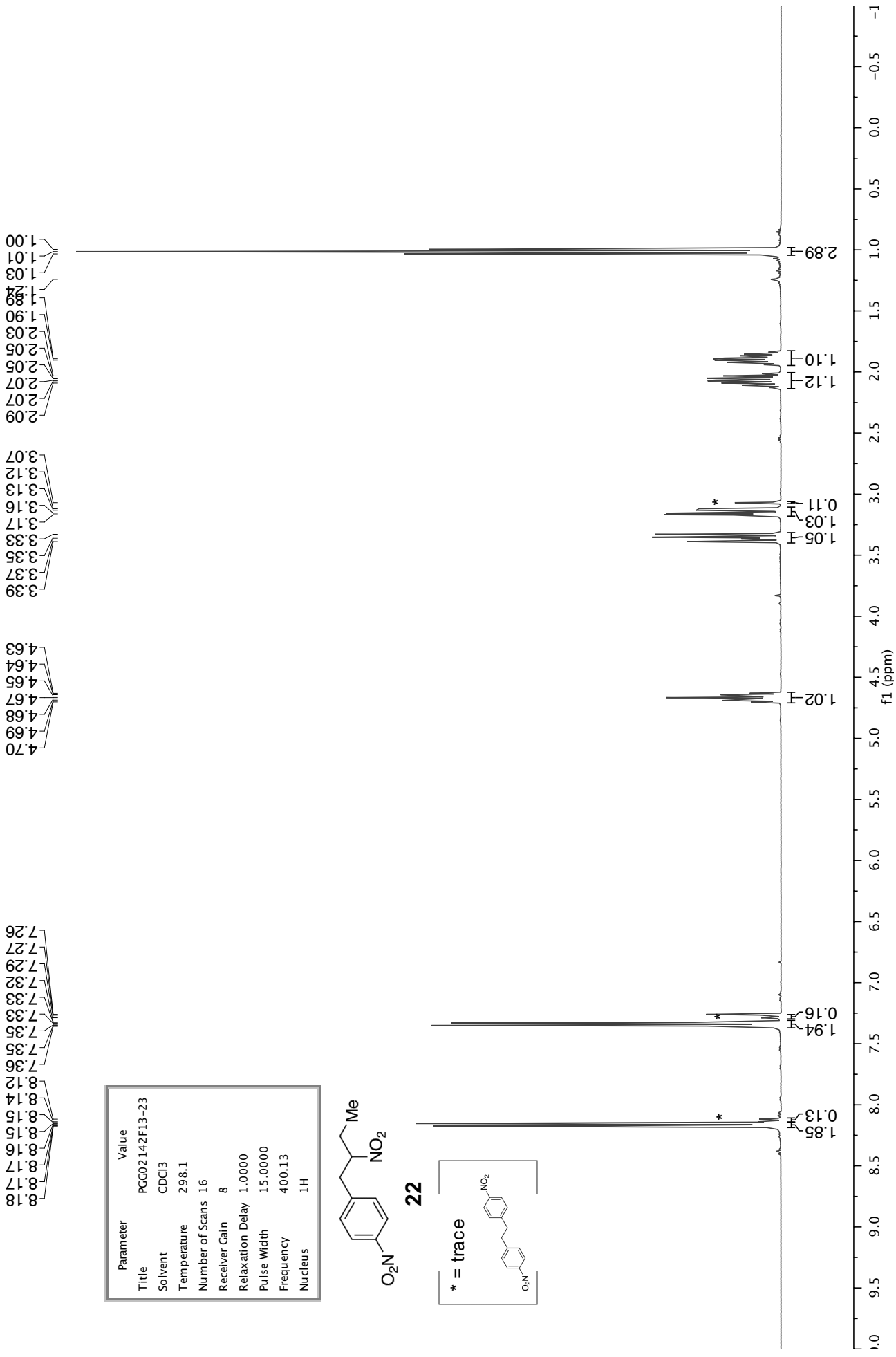

Parameter Value
Title PGG02245F9-17
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 11
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
Me
NO2
F3C
21
7.58
7.56
7.29
7.27
4.68
4.67
4.66
4.65
4.63
4.62
4.61
3.35
3.33
3.31
3.29
3.12
3.10
3.08
3.07
2.07
2.05
2.05
2.04
2.03
2.01
1.89
1.88
1.87
1.86
1.03
1.01
0.99
1.83
1.86
1.05
1.06
1.03
1.18
1.19
2.81
f1 (ppm)

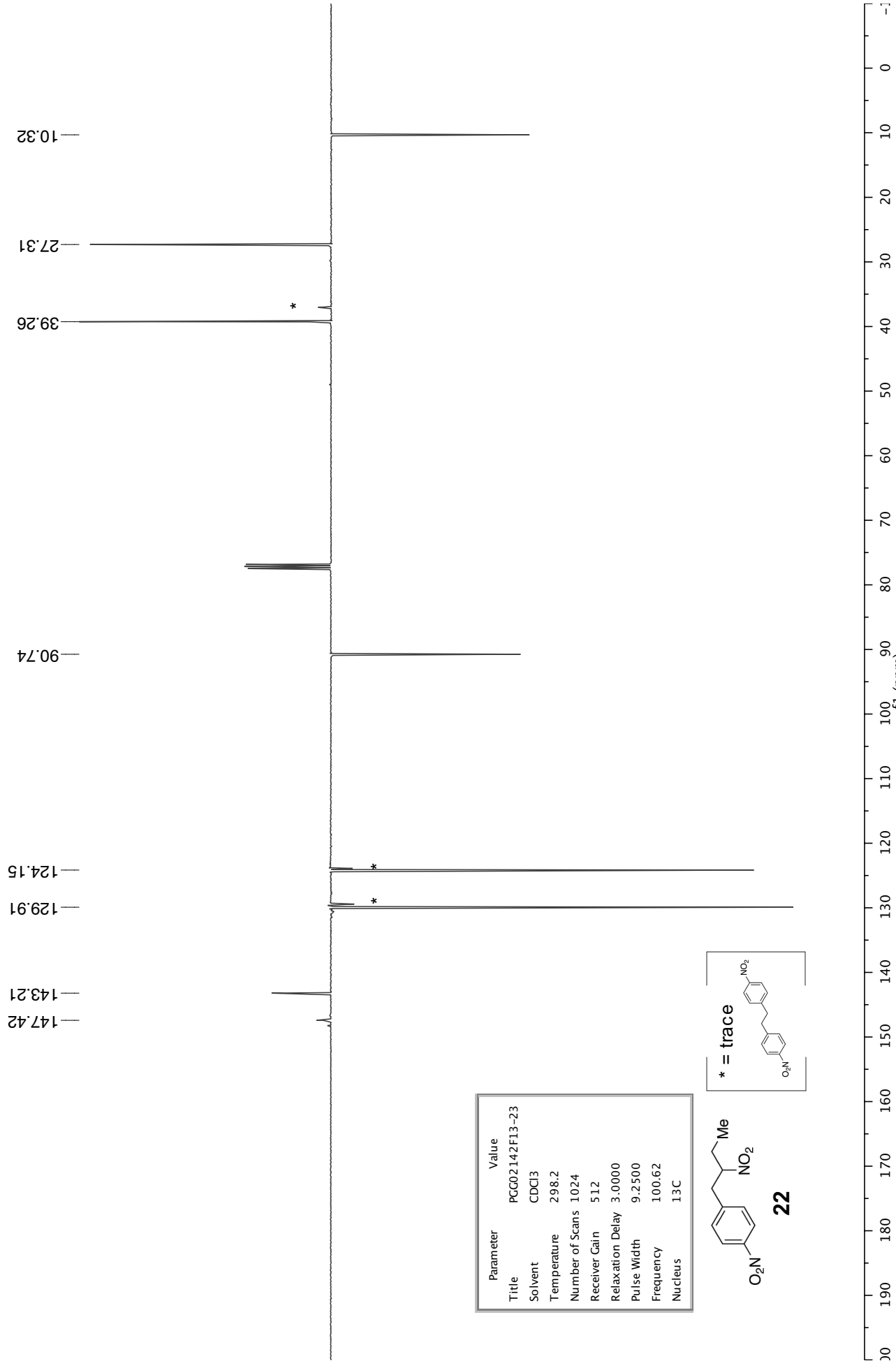

10.37
27.18
39.43
91.04
120.07
122.77
125.48
125.88
125.92
125.96
125.99
128.18
129.36
129.74
130.06
130.38
139.78
139.79
f1 (ppm)
Parameter Value
Title PGG02245F9-17
Solvent CDCl3
Temperature 298.1
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
Me
NO2
F3C
21

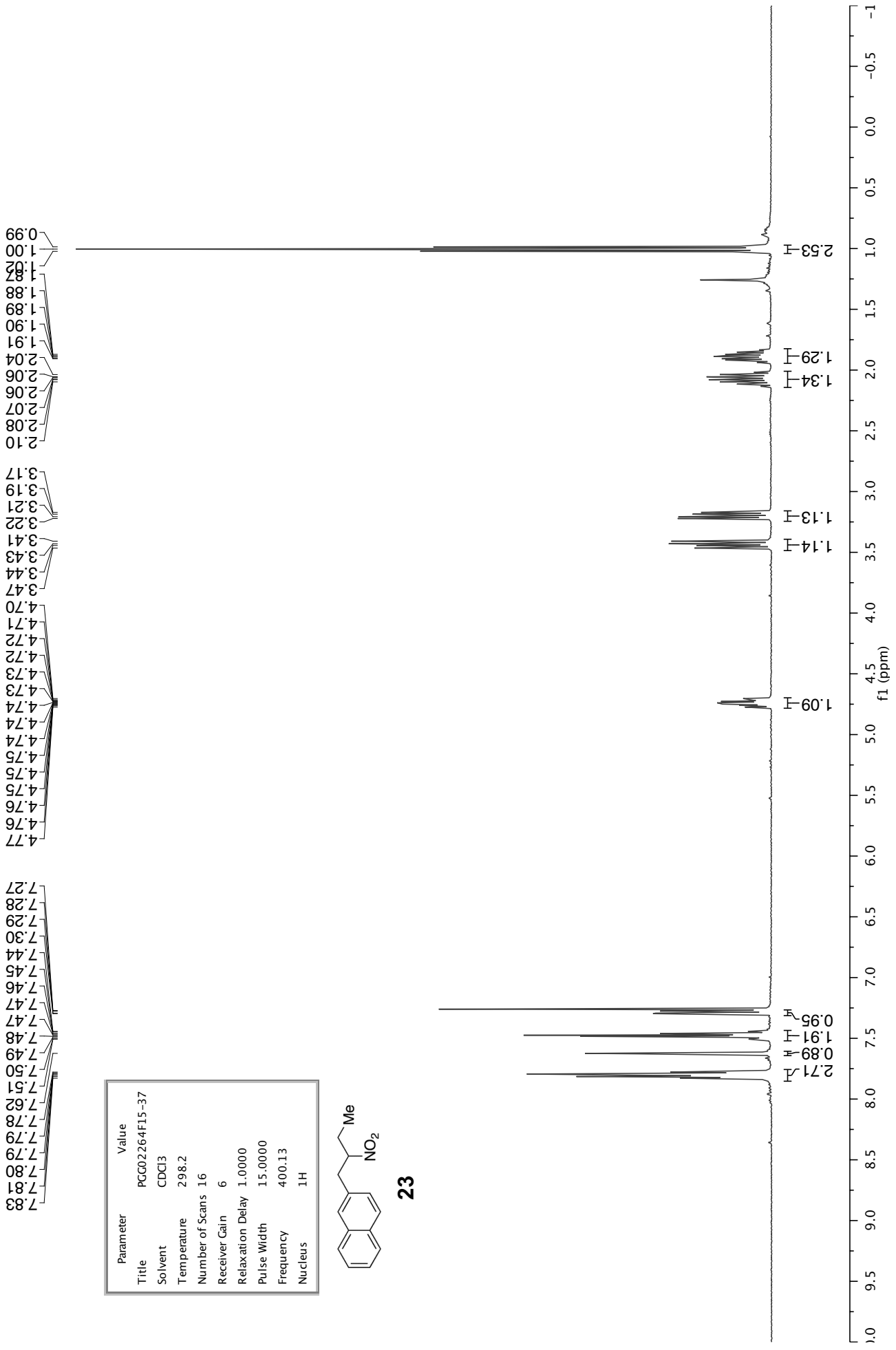
Parameter	Value
Title	PGG02245F9-17
Solvent	CDCl3
Temperature	298.2
Number of Scans	16
Receiver Gain	645
Relaxation Delay	2.0000
Pulse Width	15.0300
Frequency	376.46
Nucleus	19F

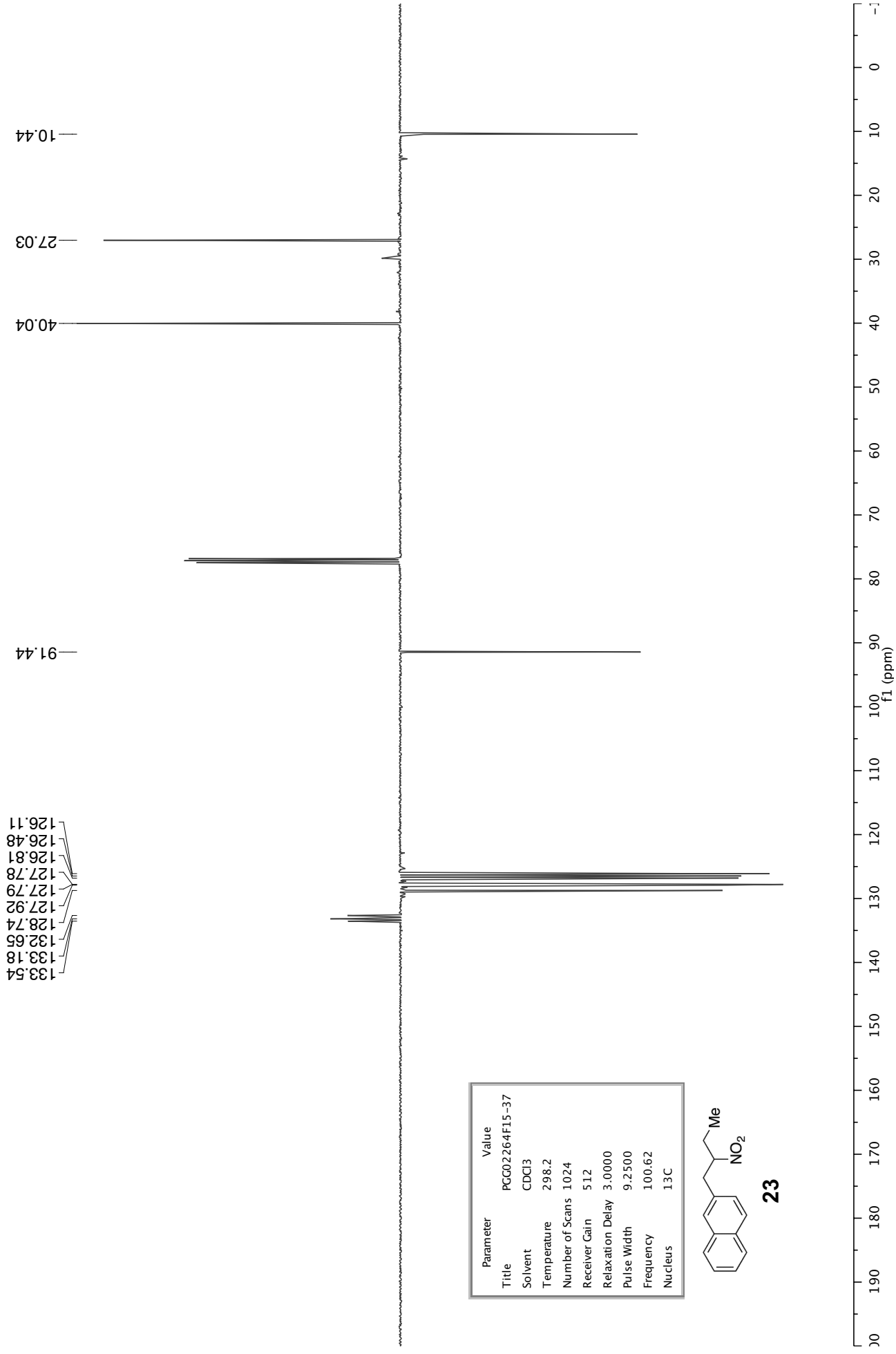


21

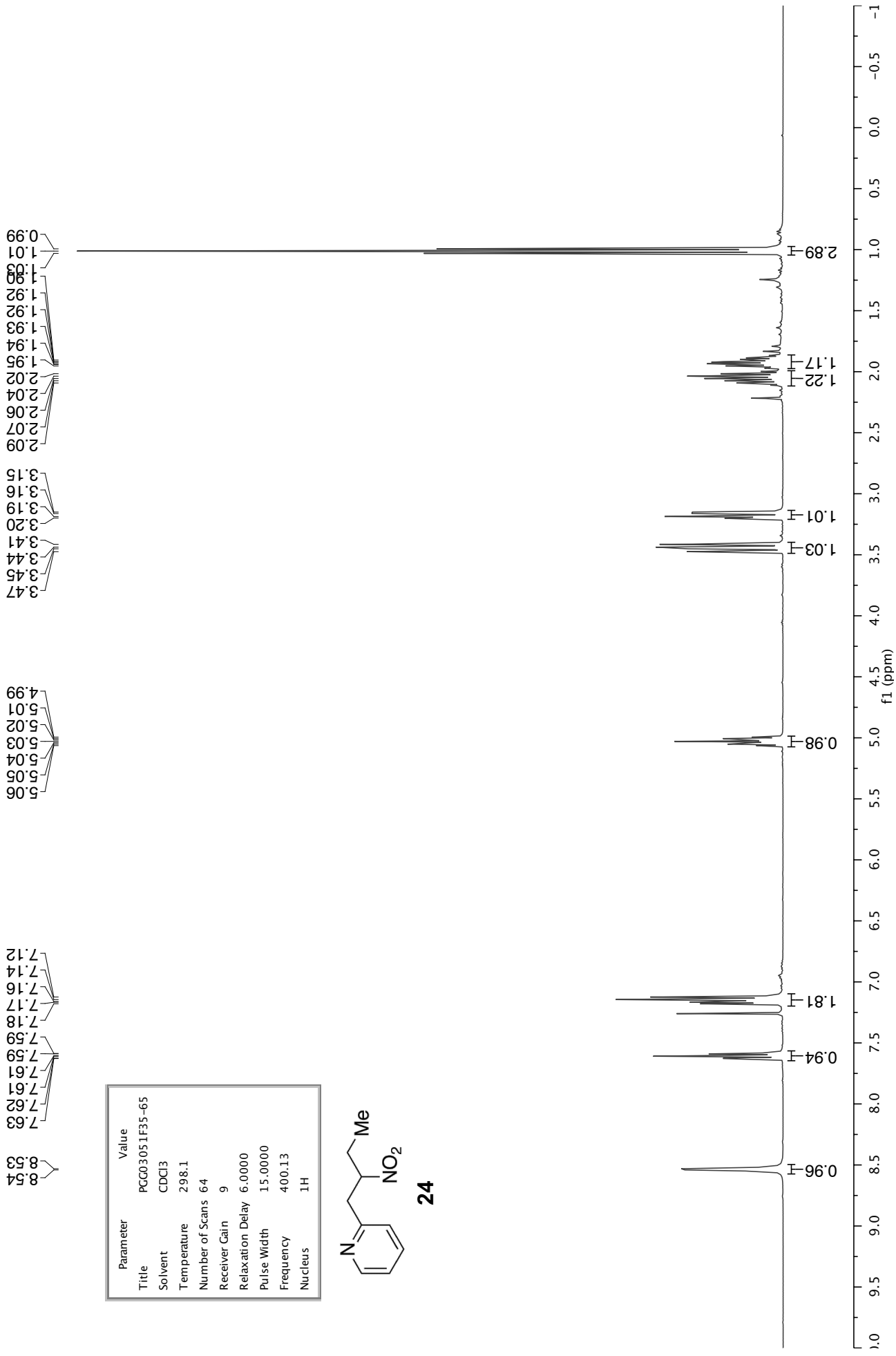

Parameter Value
Title PGG02142F13-23
Solvent CDCl3
Temperature 298.1
Number of Scans 16
Receiver Gain 8
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
Me
NO2
O2N
22
* = trace
O2N
NO2
f1 (ppm)

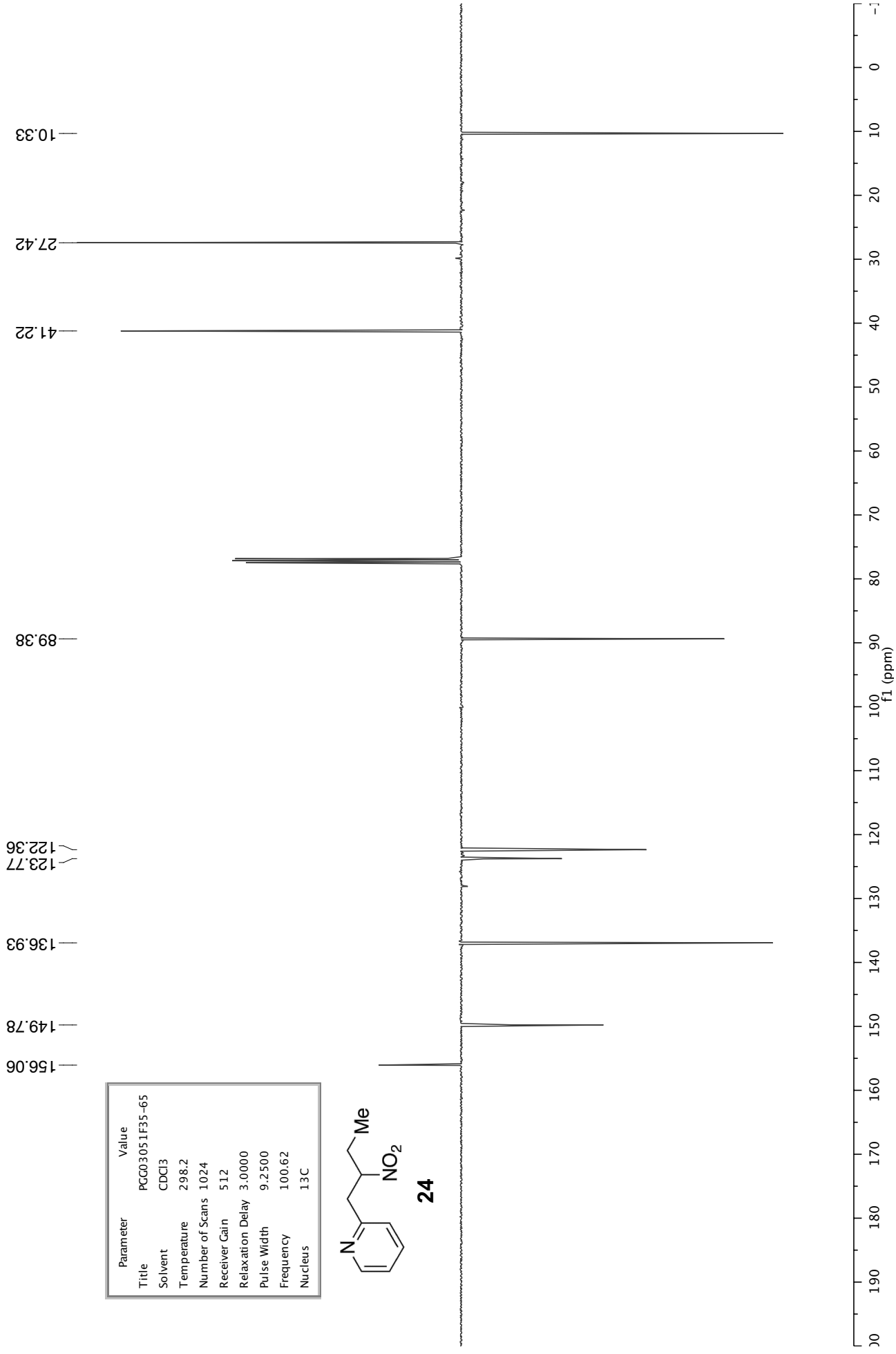

10.32
27.31
39.26
90.74
124.15
129.91
143.21
147.42
*
*
*
f1 (ppm)
Parameter Value
Title PGG02142F13-23
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
* = trace
Me
NO2
O2N
22

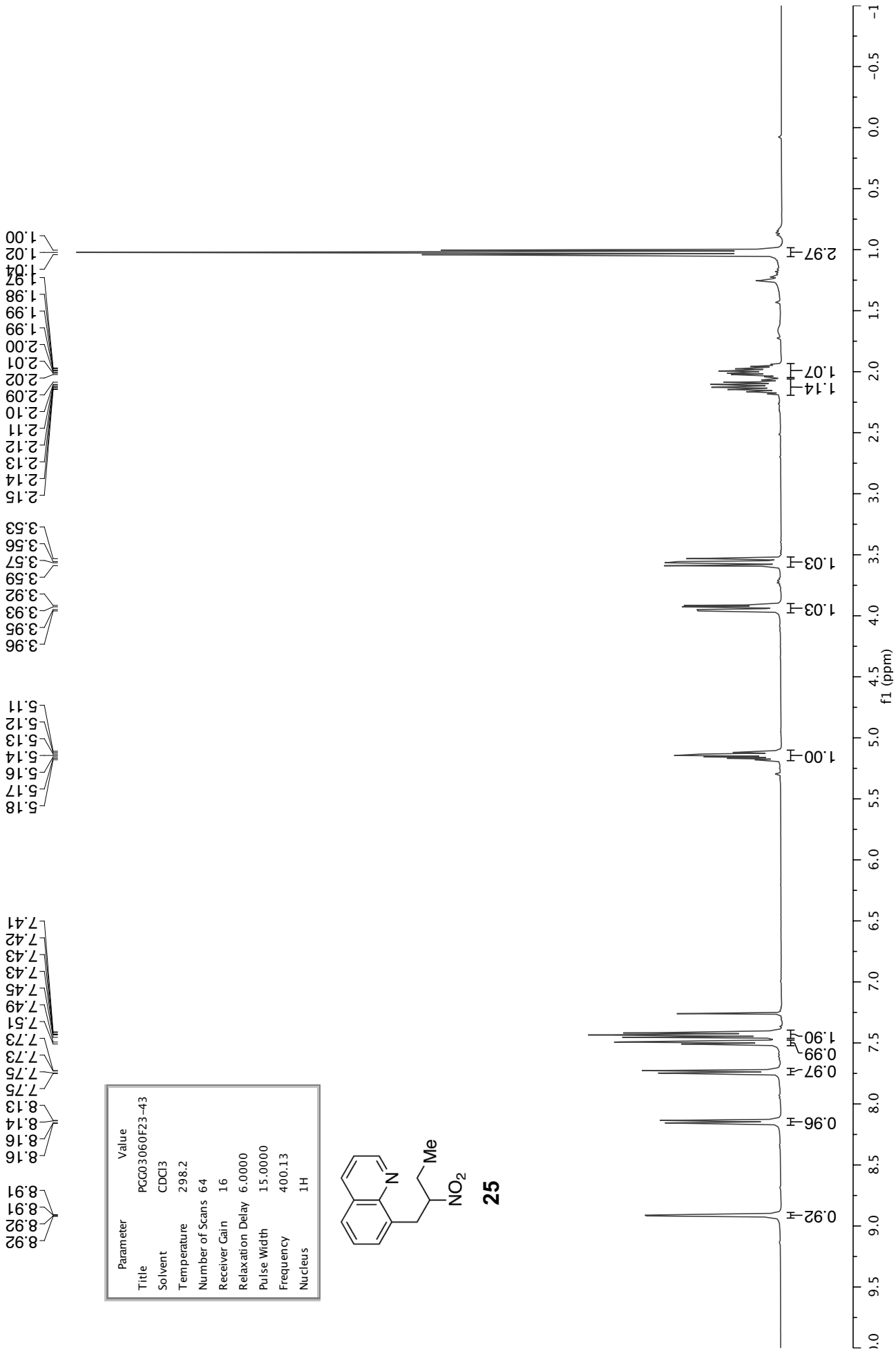

Parameter Value
Title PGG02264F15-37
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 6
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
Me
NO2
23
f1 (ppm)

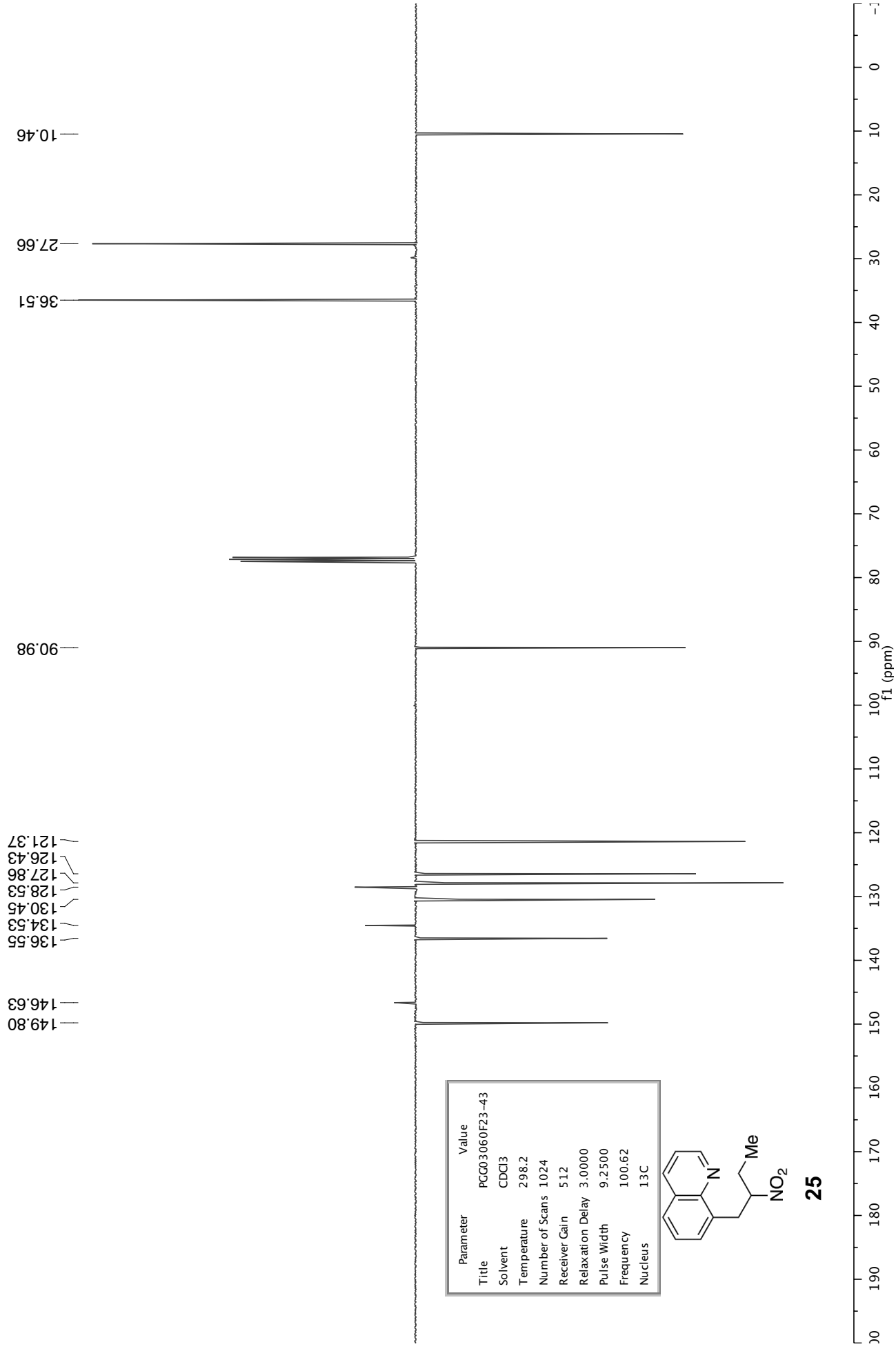

10.44
27.03
40.04
91.44
126.11
126.48
126.81
127.78
127.79
127.92
128.74
132.65
133.18
133.54
f1 (ppm)
Parameter Value
Title PGG02264F15-37
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
Me
NO2

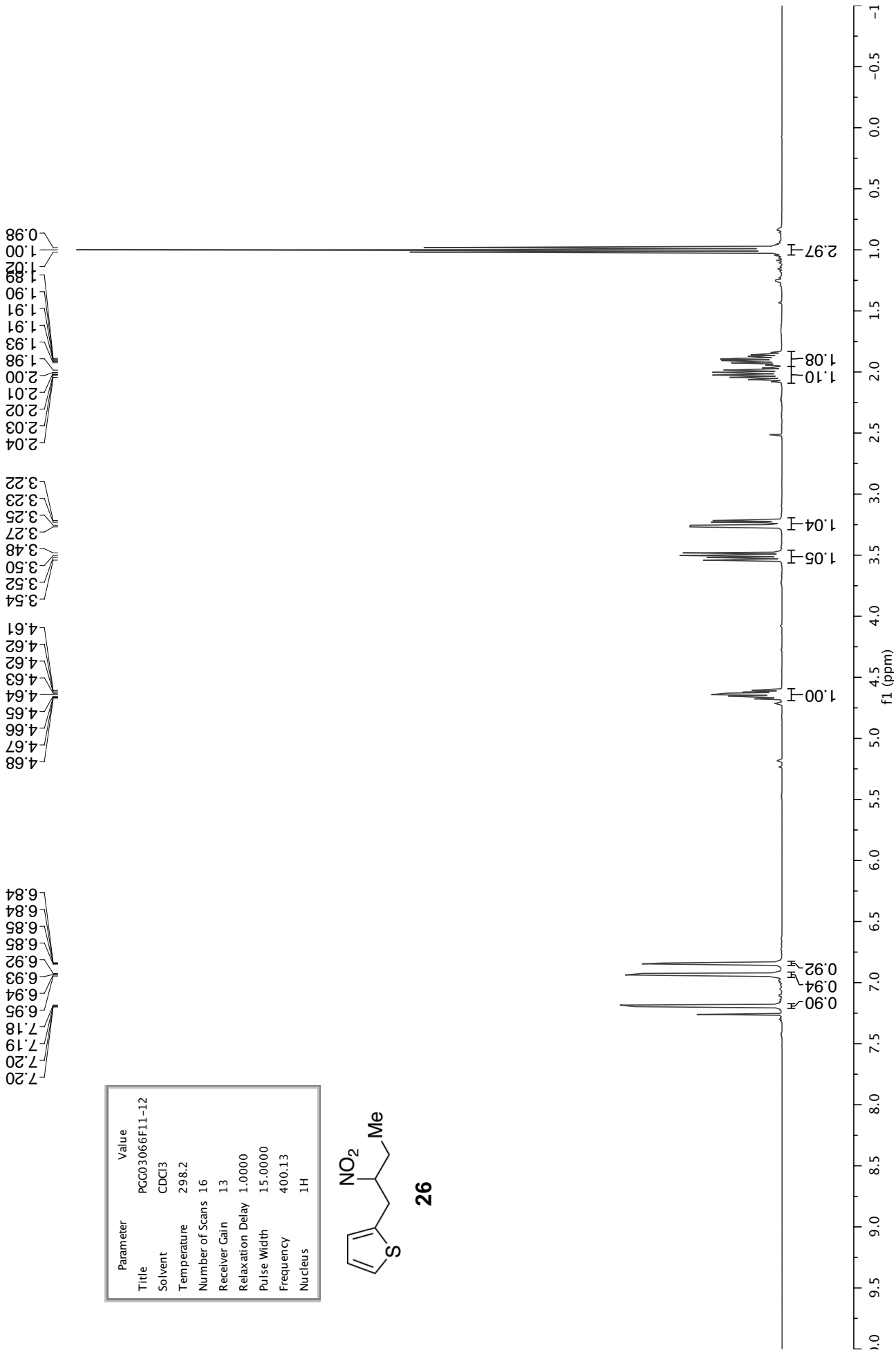
23

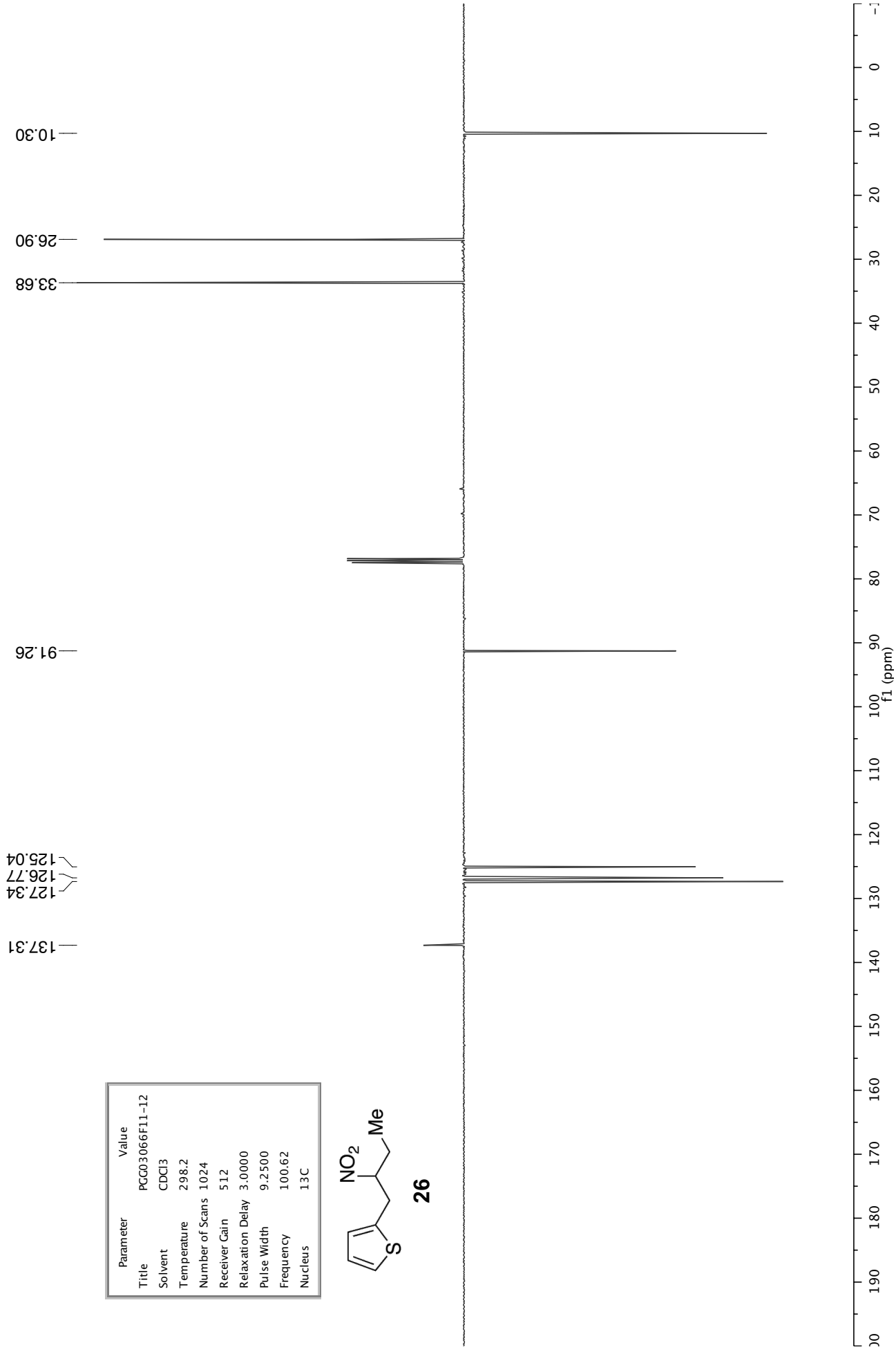

Parameter Value
Title PGG03051F35-65
Solvent CDCl3
Temperature 298.1
Number of Scans 64
Receiver Gain 9
Relaxation Delay 6.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
Me
NO2
N
24
f1 (ppm)

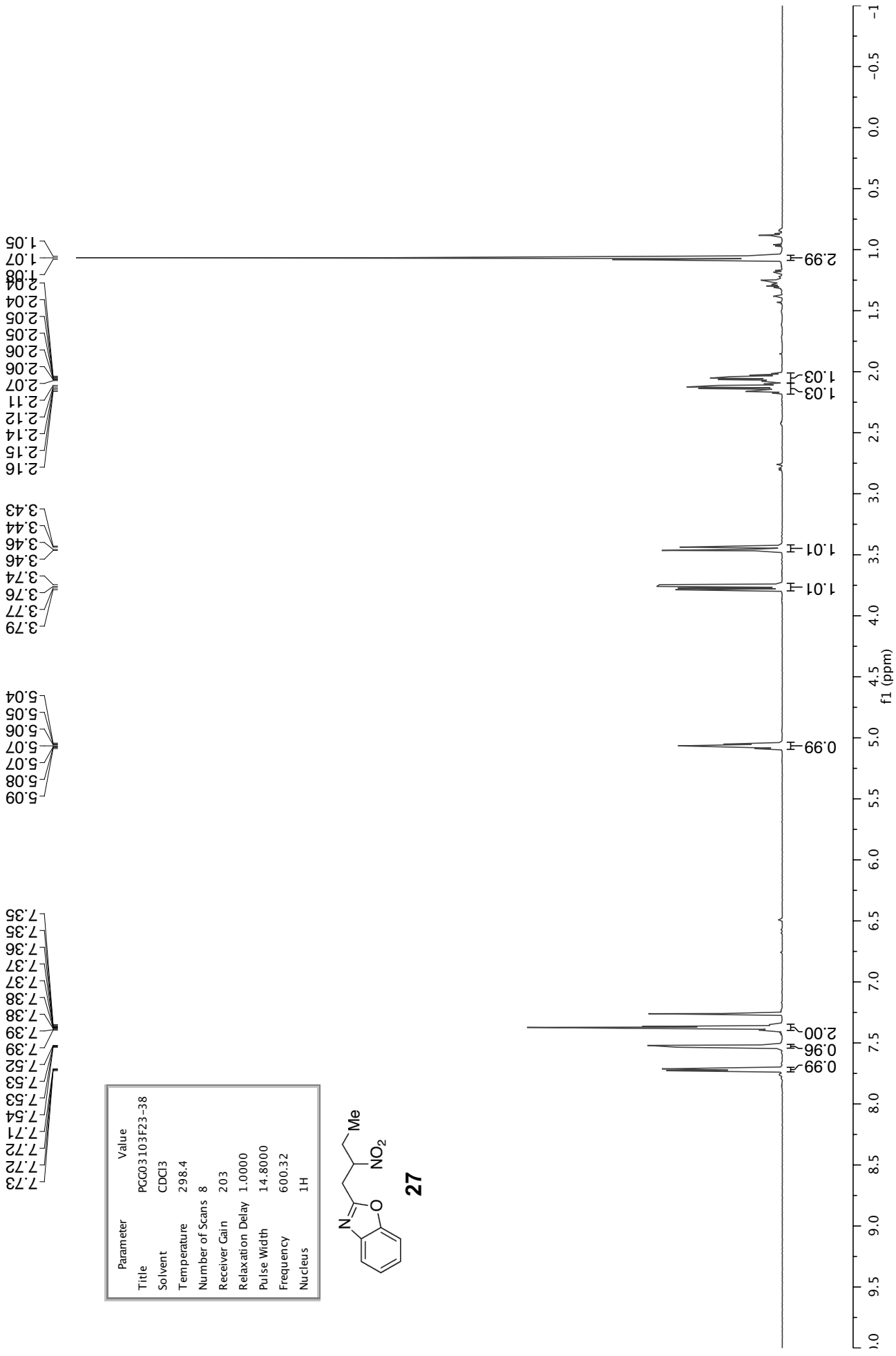

10.33
27.42
41.22
89.38
122.36
123.77
136.93
149.78
156.06
Parameter Value
Title PGG03051F35-65
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
N
NO2
Me
24
f1 (ppm)

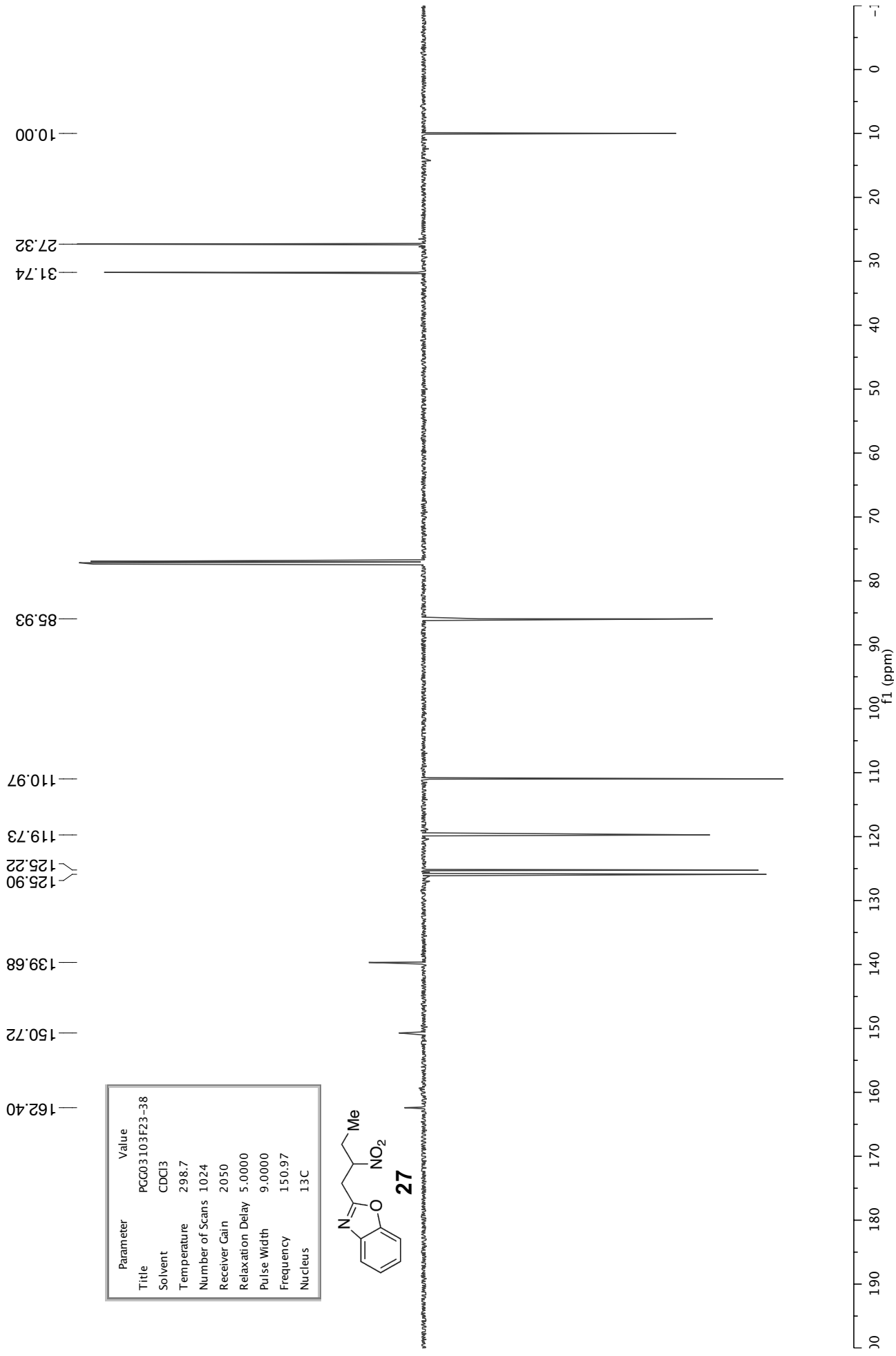

Parameter Value
Title PGG03060F23-43
Solvent CDCl3
Temperature 298.2
Number of Scans 64
Receiver Gain 16
Relaxation Delay 6.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
N
Me
NO2
25
f1 (ppm)

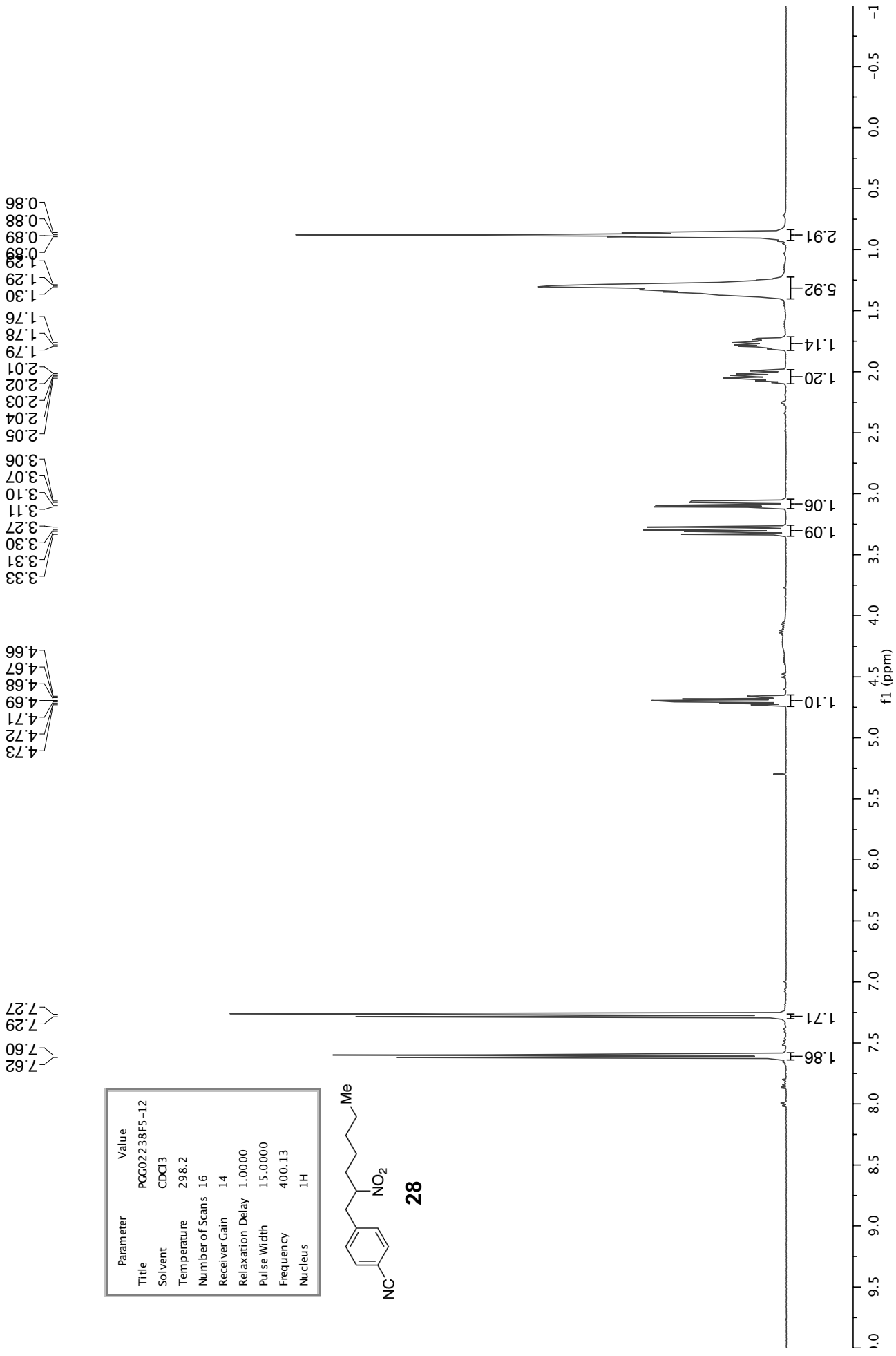

10.46
27.66
36.51
90.98
121.37
126.43
127.86
128.53
130.45
134.53
136.55
146.63
149.80
f1 (ppm)
Parameter Value
Title PGC03060F23-43
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
N
Me
NO2
25

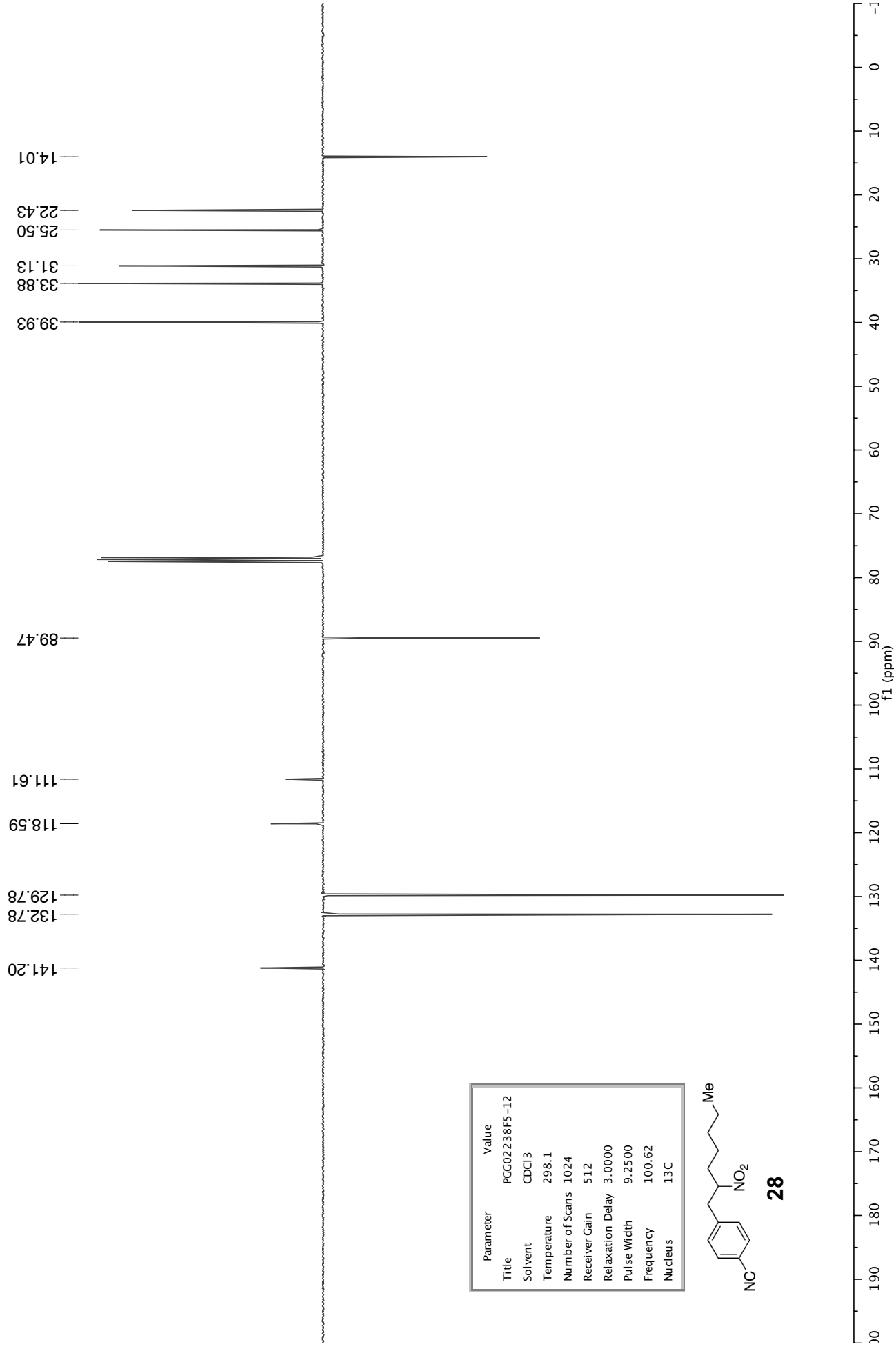

Parameter Value
Title PGG03066F11-12
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 13
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
NO2
Me
S
26
f1 (ppm)

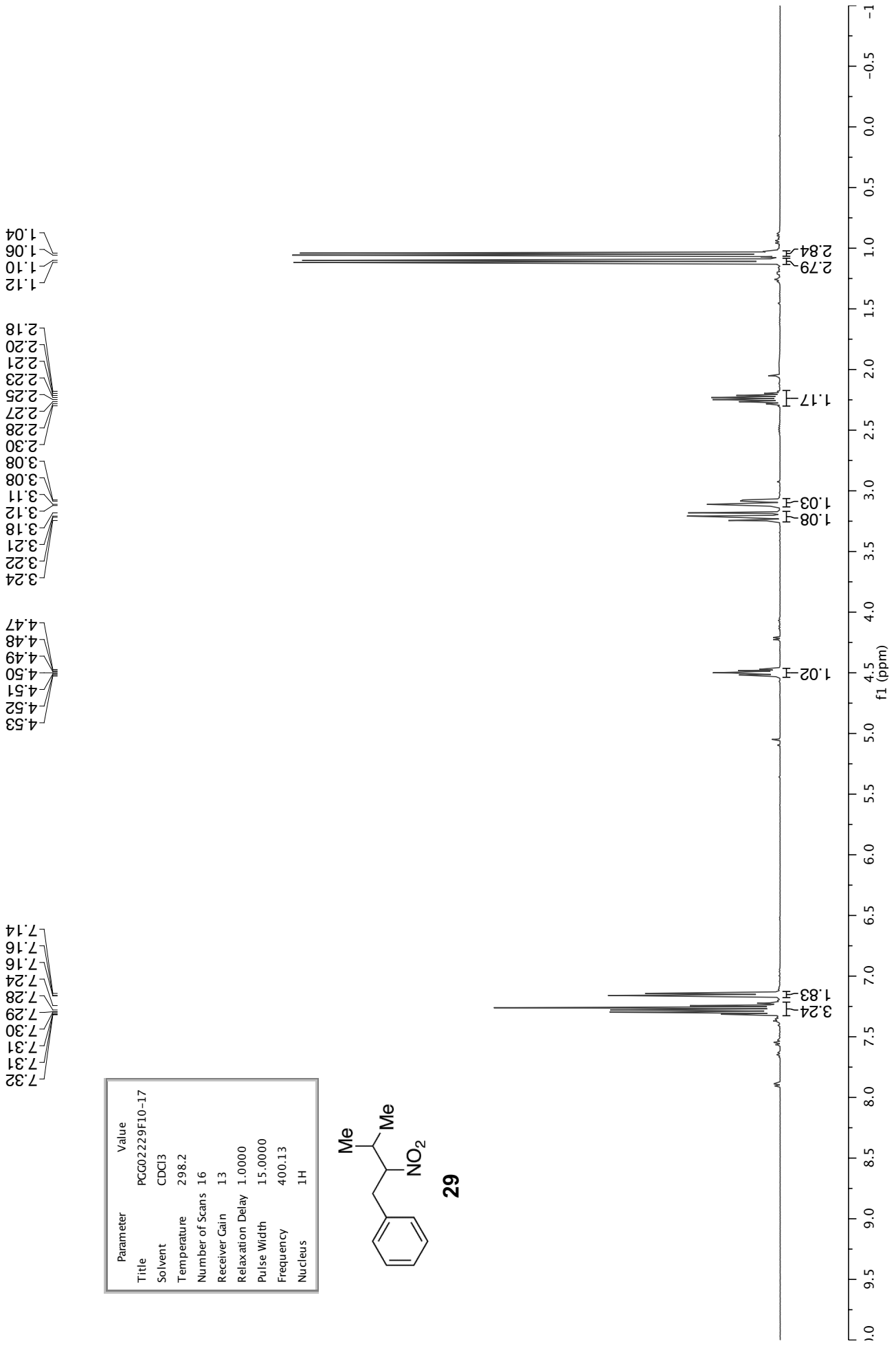

10.30
26.90
33.68
91.26
125.04
126.77
127.34
137.31
f1 (ppm)
Parameter Value
Title PGG03066F11-12
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
NO2
Me
S
26

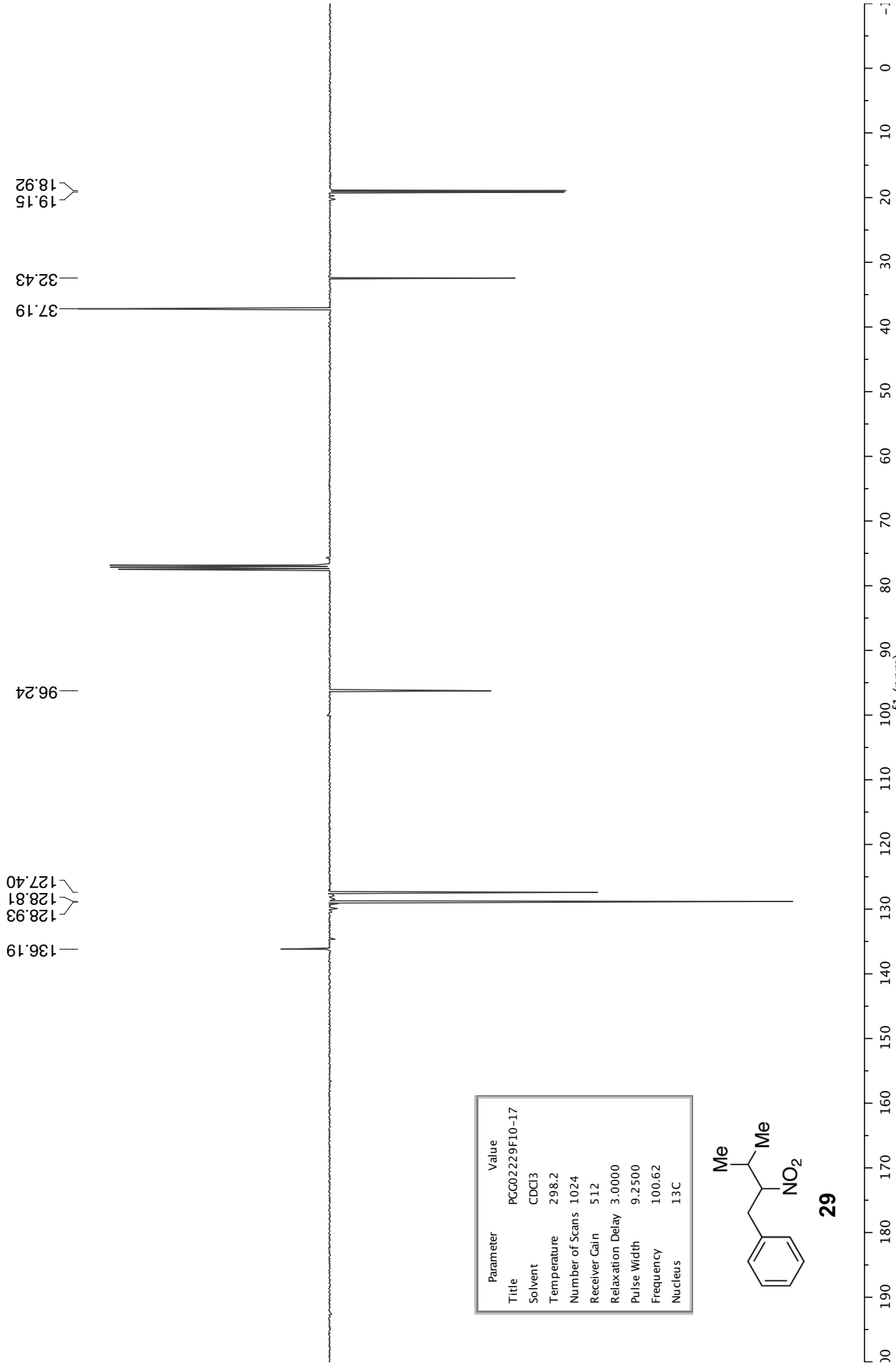

Parameter Value
Title PGG03103F23-38
Solvent CDCl3
Temperature 298.4
Number of Scans 8
Receiver Gain 203
Relaxation Delay 1.0000
Pulse Width 14.8000
Frequency 600.32
Nucleus 1H
Me
NO2
N
O
27
f1 (ppm)

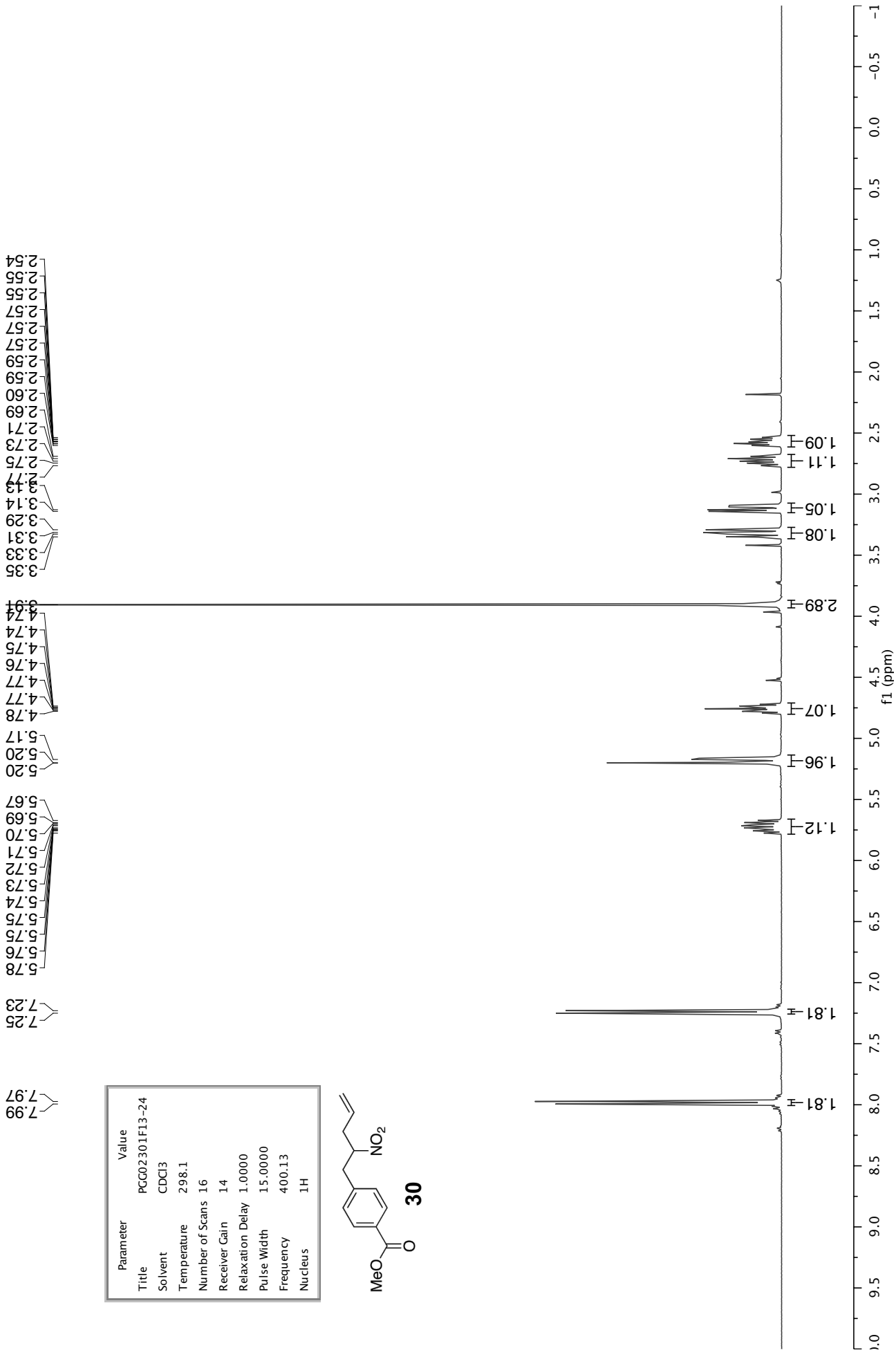

10.00
27.32
31.74
85.93
110.97
119.73
125.22
125.90
139.68
150.72
162.40
f1 (ppm)
Parameter Value
Title PGG03103F23-38
Solvent CDCl3
Temperature 298.7
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 9.0000
Frequency 150.97
Nucleus 13C
Me
NO2
N
O
27

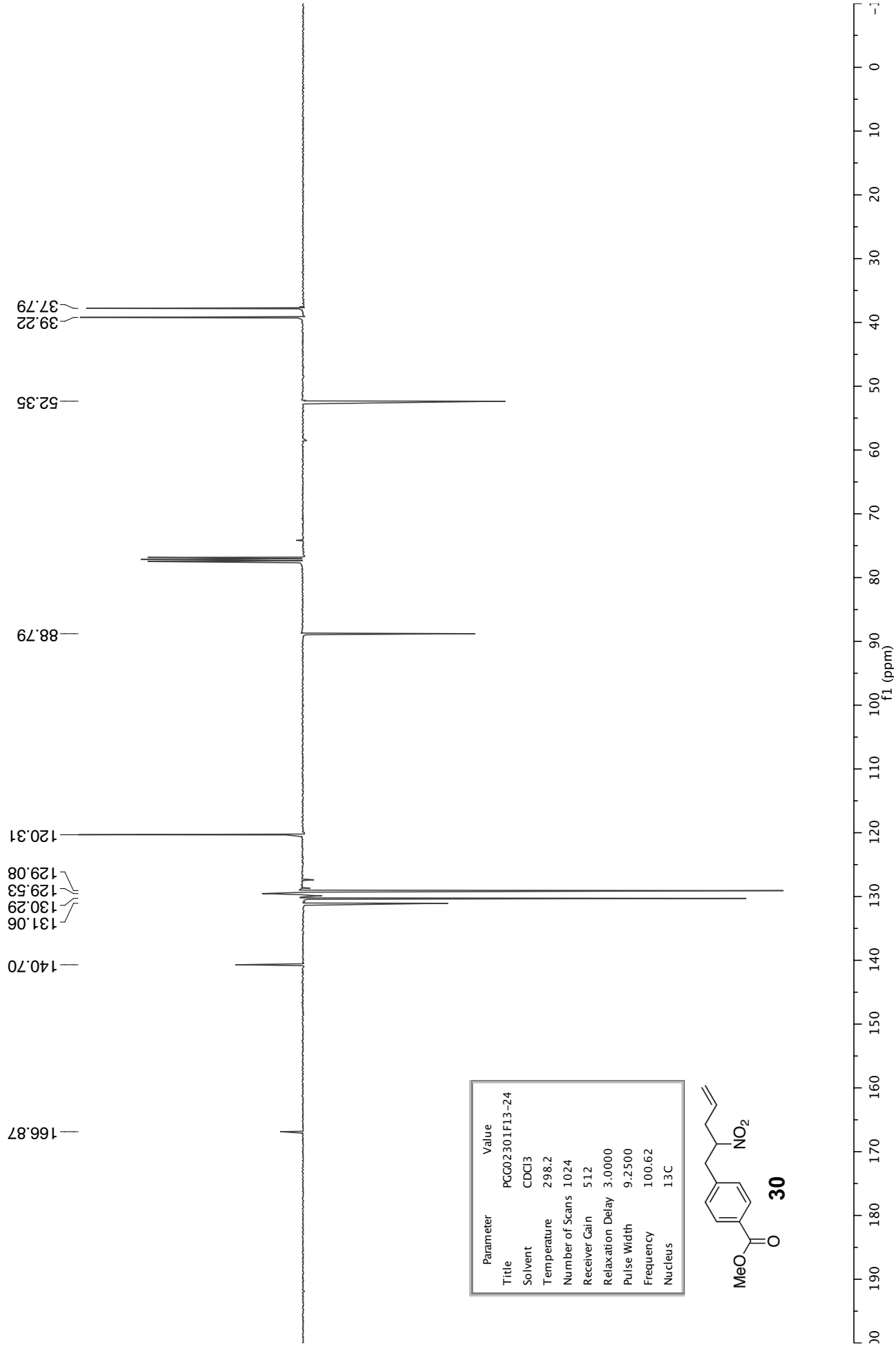

Parameter Value
Title PGG02238F5-12
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 14
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
Me
NO2
NC
28
7.62
7.60
7.29
7.27
4.73
4.72
4.71
4.69
4.68
4.67
4.66
3.33
3.31
3.30
3.27
3.11
3.10
3.07
3.06
2.05
2.04
2.03
2.02
2.01
1.79
1.78
1.76
1.30
1.29
0.89
0.88
0.86
1.71
1.86
1.10
1.09
1.06
1.20
1.14
5.92
2.91
f1 (ppm)

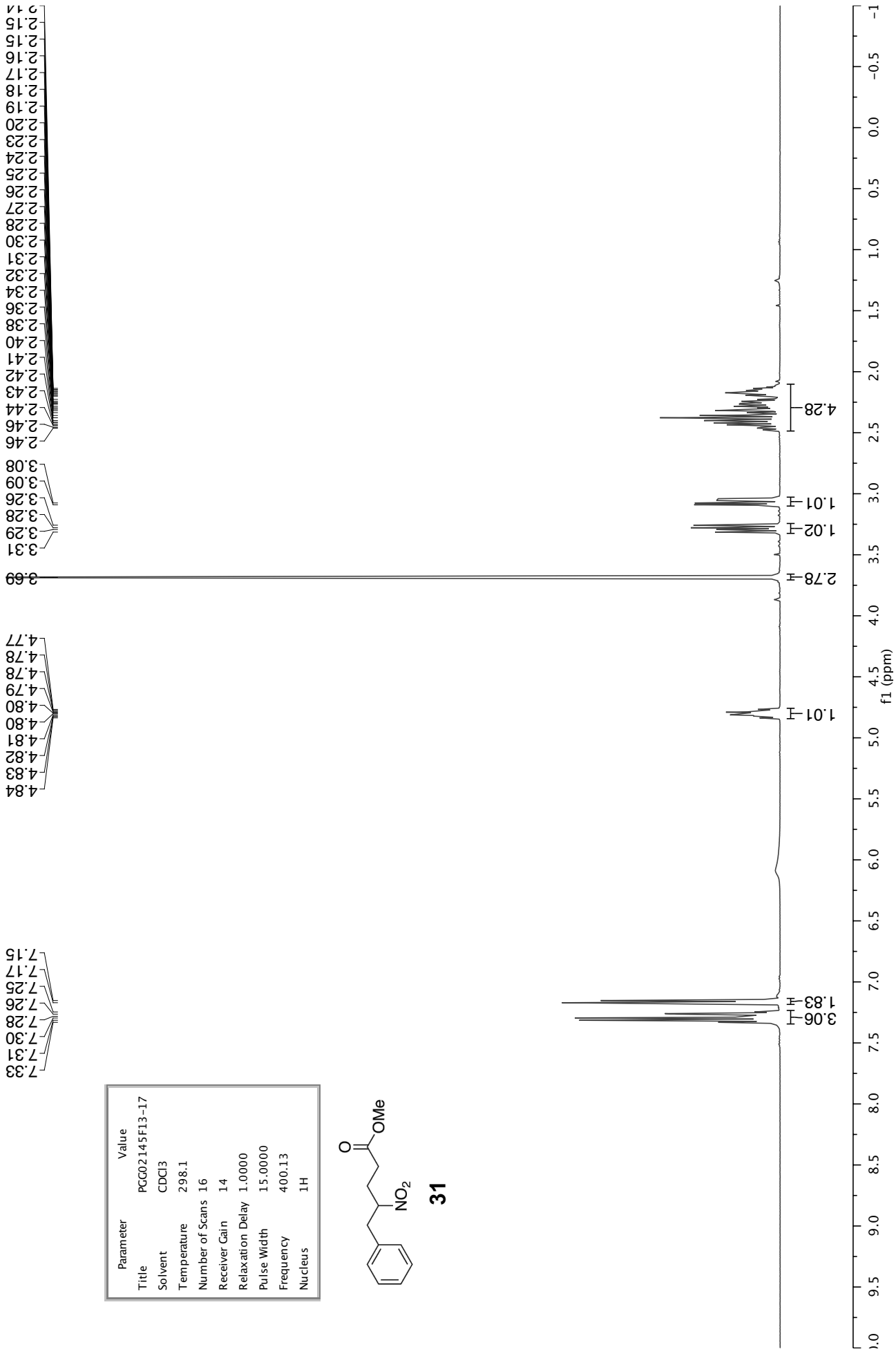

14.01
22.43
25.50
31.13
33.88
39.93
89.47
111.61
118.59
129.78
132.78
141.20
f1 (ppm)
Parameter Value
Title PGG02238F5-12
Solvent CDCl3
Temperature 298.1
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
Me
NO2
NC
28

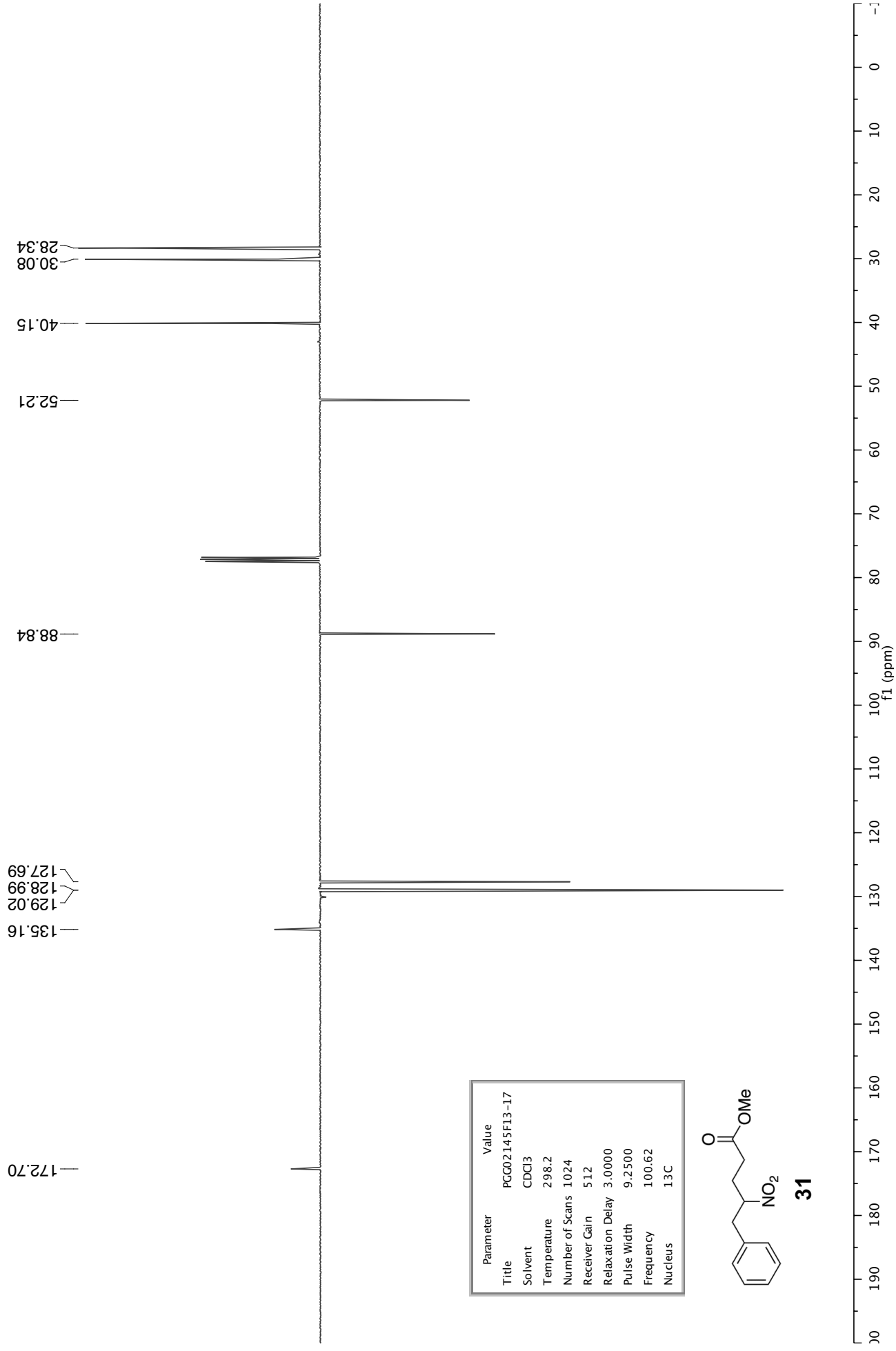

Parameter Value
Title PGG02229F10-17
Solvent CDCl3
Temperature 298.2
Number of Scans 16
Receiver Gain 13
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
Me
Me
NO2
29
7.32
7.31
7.31
7.30
7.29
7.28
7.24
7.16
7.16
7.14
4.53
4.52
4.51
4.50
4.49
4.48
4.47
3.24
3.22
3.21
3.18
3.12
3.11
3.08
3.08
2.30
2.28
2.27
2.25
2.23
2.21
2.20
2.18
1.12
1.10
1.06
1.04
3.24
1.83
1.02
1.08
1.03
1.17
2.84
2.79
f1 (ppm)

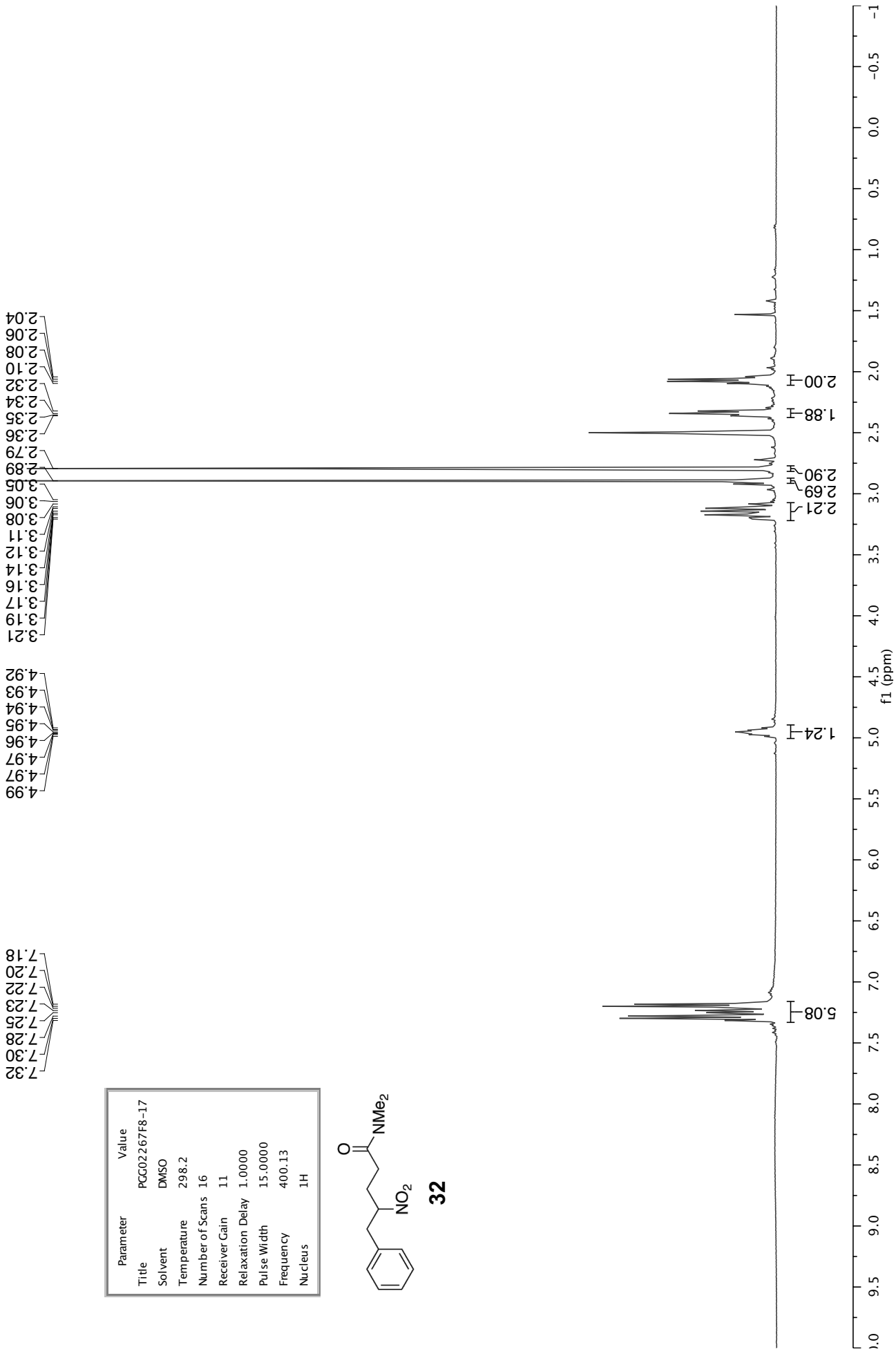

18.92
19.15
32.43
37.19
96.24
127.40
128.81
128.93
136.19
f1 (ppm)
Parameter Value
Title PGG02229F10-17
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
Me
Me
NO2
29

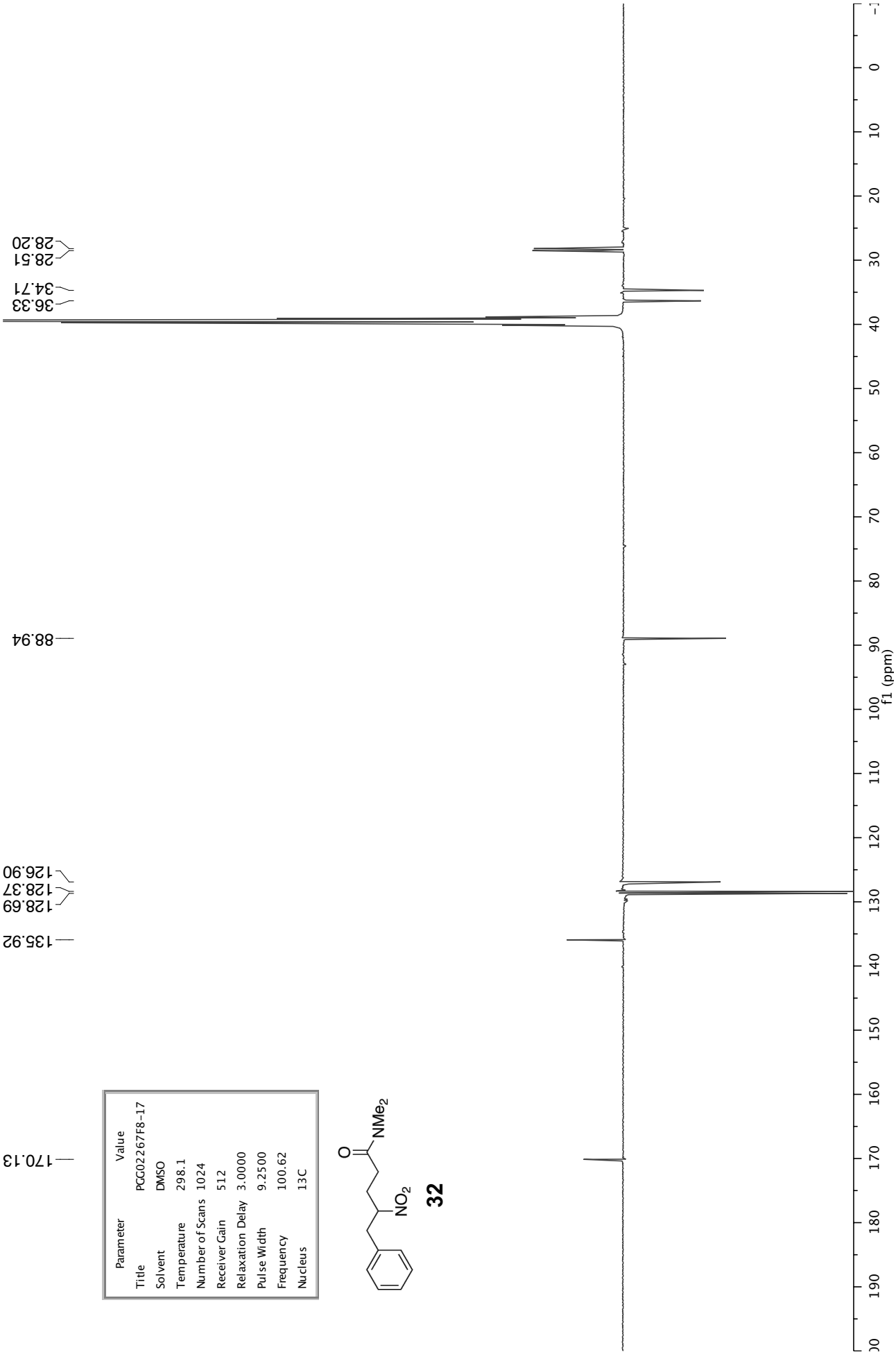

Parameter Value
Title PGG02301F13-24
Solvent CDCl3
Temperature 298.1
Number of Scans 16
Receiver Gain 14
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
MeO
O
NO2
30
f1 (ppm)


37.79
39.22
52.35
88.79
120.31
129.08
129.53
130.29
131.06
140.70
166.87
f1 (ppm)
Parameter Value
Title PGG02301F13-24
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
MeO
O
NO2
30

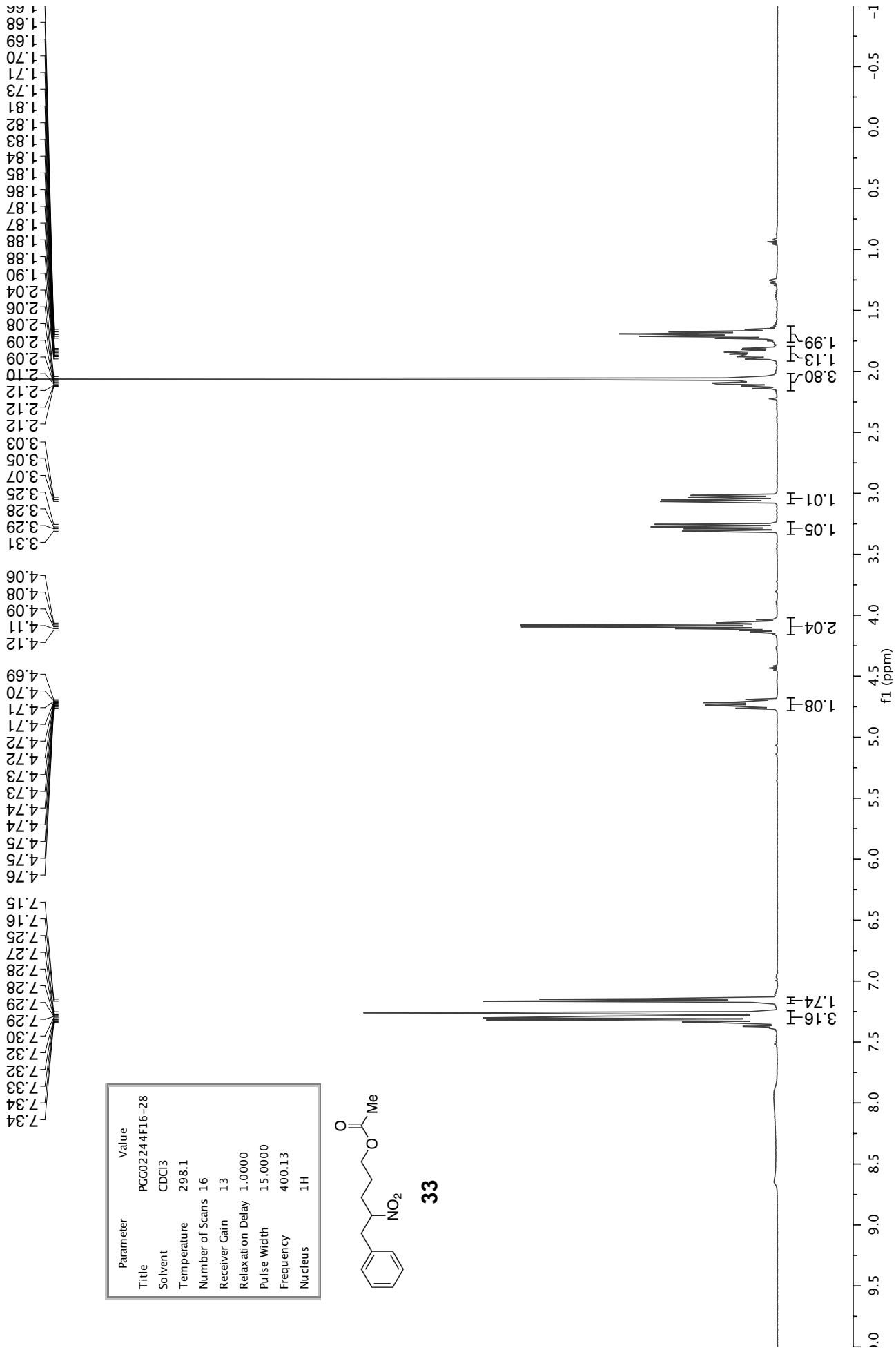

Parameter Value
Title PGG02145F13-17
Solvent CDCl3
Temperature 298.1
Number of Scans 16
Receiver Gain 14
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
O
OMe
NO2
31
7.33
7.31
7.30
7.28
7.26
7.25
7.17
7.15
4.84
4.83
4.82
4.81
4.80
4.80
4.79
4.78
4.78
4.77
3.69
3.31
3.29
3.28
3.26
3.09
3.08
2.46
2.46
2.44
2.43
2.42
2.41
2.40
2.38
2.36
2.34
2.32
2.31
2.30
2.28
2.27
2.26
2.25
2.24
2.23
2.20
2.19
2.18
2.17
2.16
2.15
2.15
2.14
3.06
1.83
1.01
2.78
1.02
1.01
4.28
f1 (ppm)

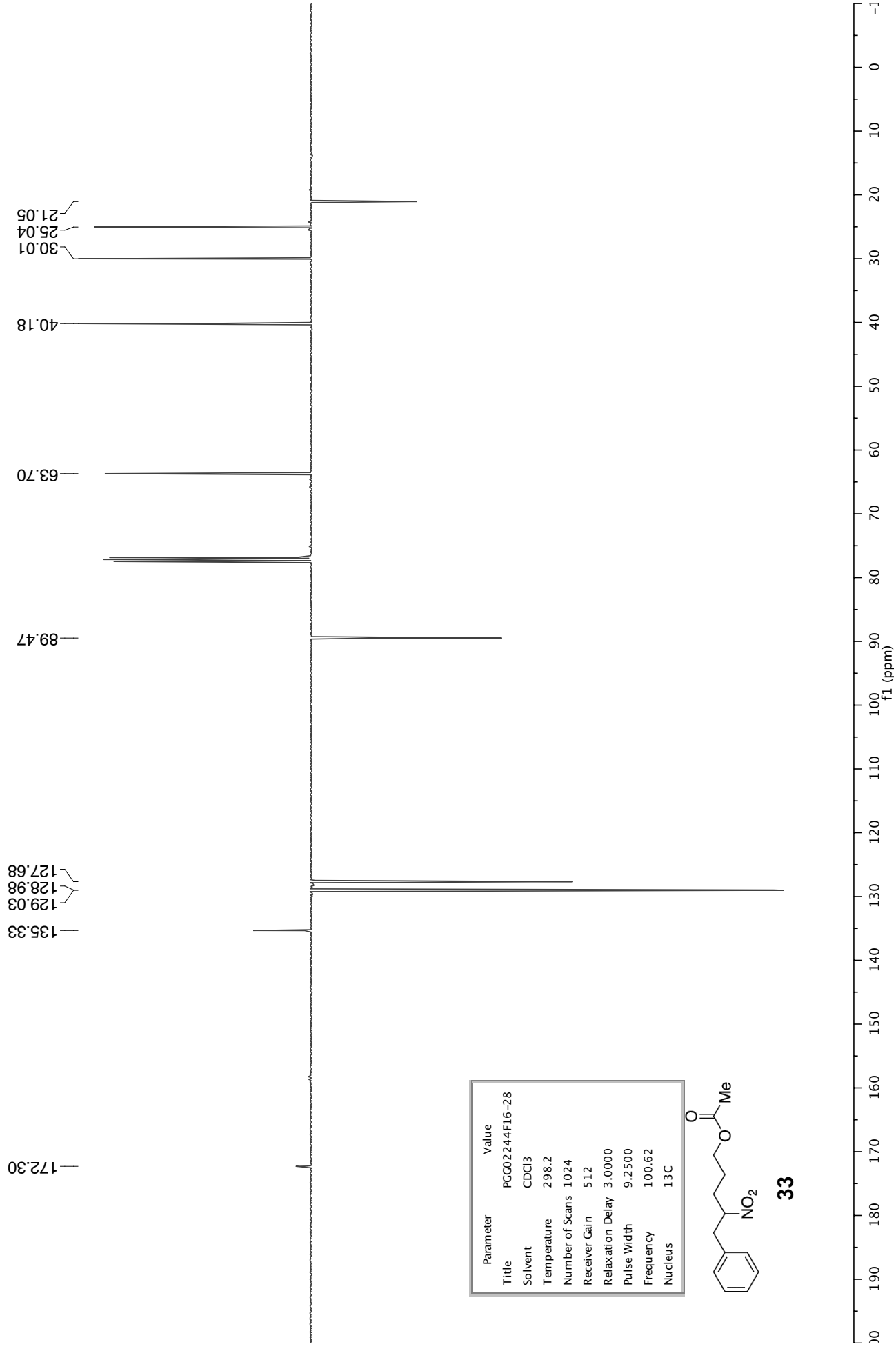

28.34
30.08
40.15
52.21
88.84
127.69
128.99
129.02
135.16
172.70
f1 (ppm)
Parameter Value
Title PGG02145F13-17
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
O
OMe
NO2
31


Parameter Value
Title PGG02267F8-17
Solvent DMSO
Temperature 298.2
Number of Scans 16
Receiver Gain 11
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
O
NMe2
NO2
32
7.32
7.30
7.28
7.25
7.23
7.22
7.20
7.18
4.99
4.97
4.97
4.96
4.95
4.94
4.93
4.92
3.21
3.19
3.17
3.16
3.14
3.12
3.11
3.08
3.06
3.05
2.89
2.79
2.36
2.35
2.34
2.32
2.10
2.08
2.06
2.04
5.08
1.24
2.21
2.69
2.90
1.88
2.00
f1 (ppm)

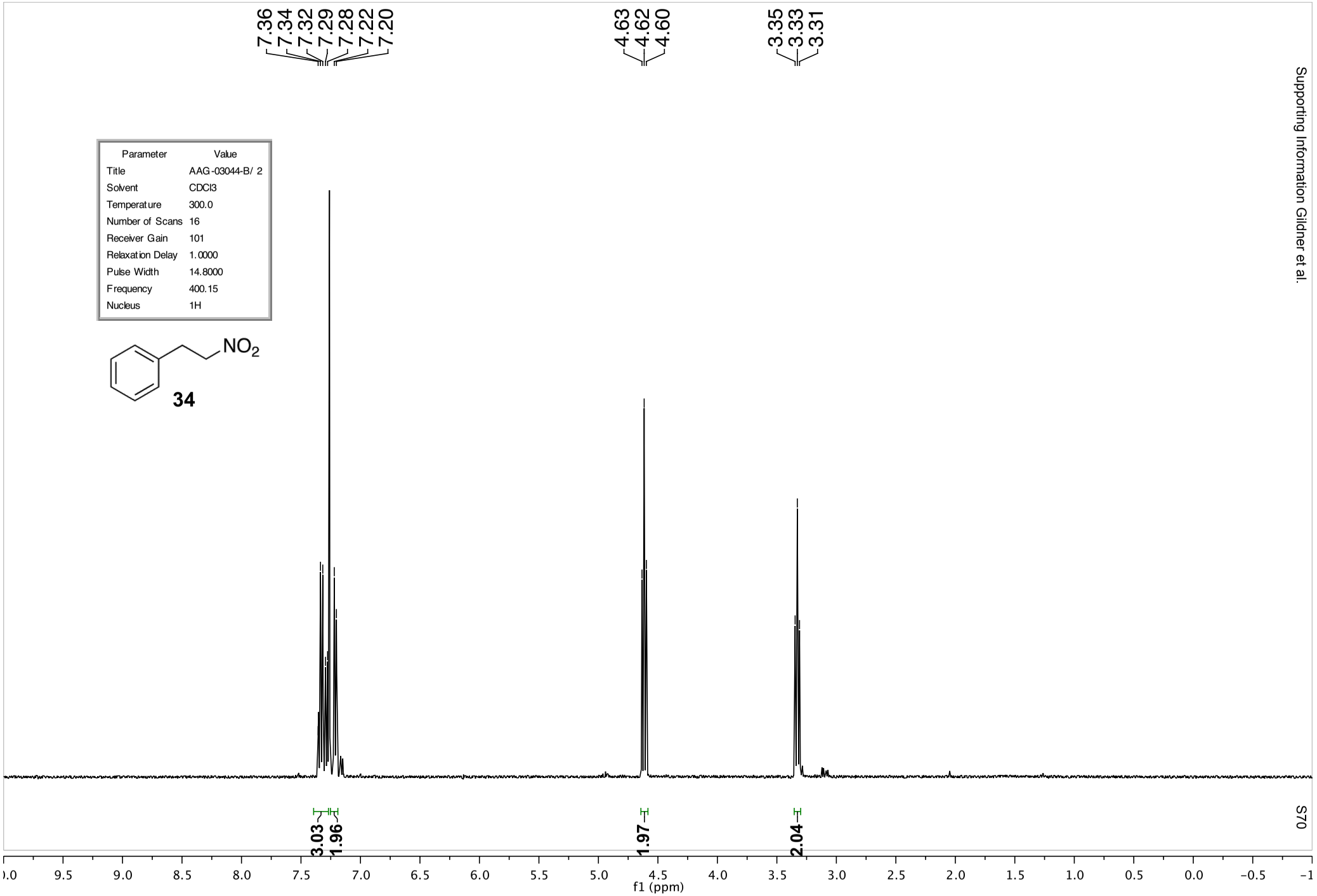

28.20
28.51
34.71
36.33
88.94
126.90
128.37
128.69
135.92
170.13
f1 (ppm)
Parameter Value
Title PGG02267F8-17
Solvent DMSO
Temperature 298.1
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
O
NMe2
NO2

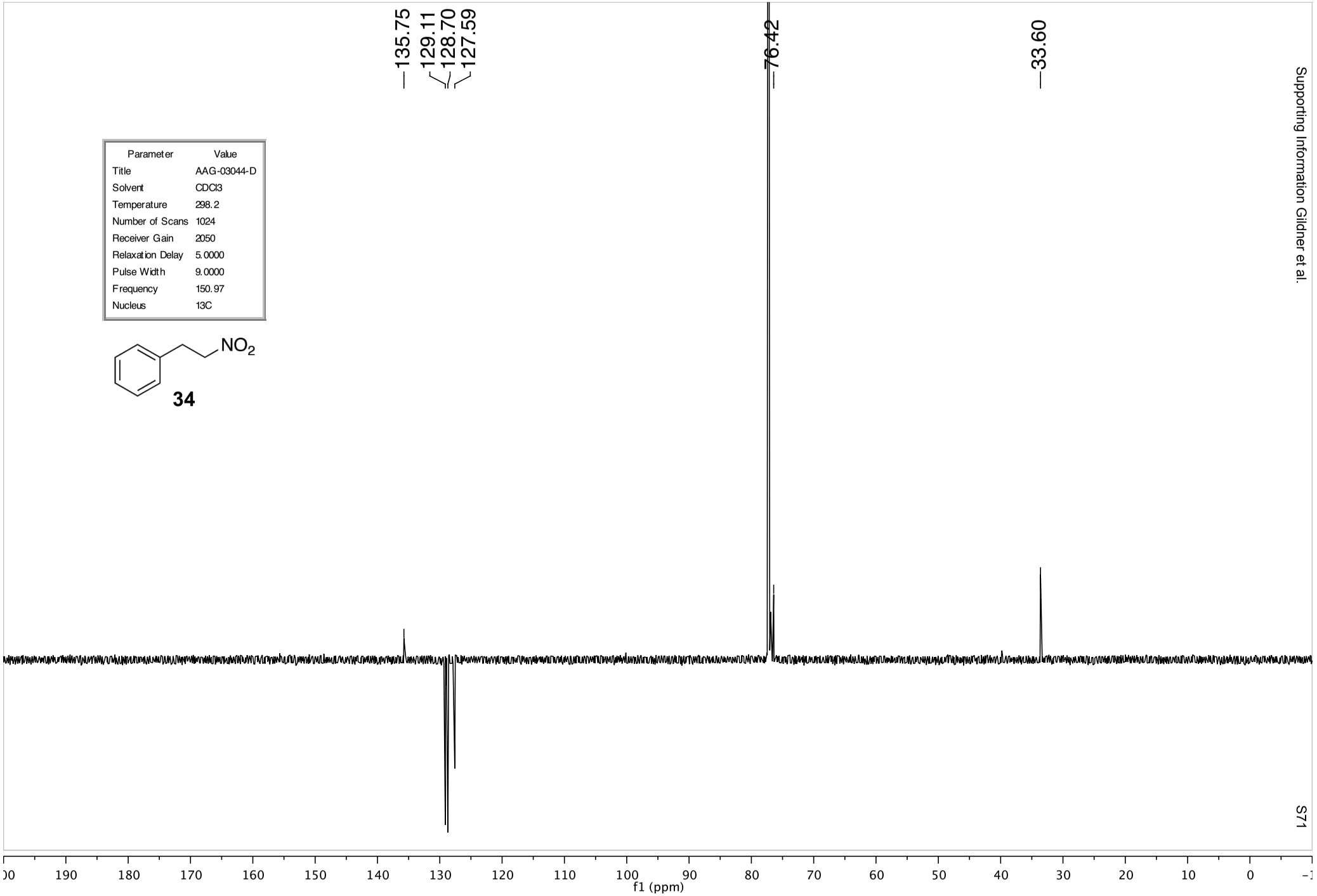
32


Parameter Value
Title PGG02244F16-28
Solvent CDCl3
Temperature 298.1
Number of Scans 16
Receiver Gain 13
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
O
O
Me
NO2
33
3.16
1.74
1.08
2.04
1.05
1.01
3.80
1.13
1.99
f1 (ppm)


172.30
135.33
129.03
128.98
127.68
89.47
63.70
40.18
30.01
25.04
21.05
f1 (ppm)
Parameter Value
Title PGG02244F16-28
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
O
O
Me
NO2

33


7.36
7.34
7.32
7.29
7.28
7.22
7.20
4.63
4.62
4.60
3.35
3.33
3.31
Parameter Value
Title AAG-03044-B/ 2
Solvent CDCl3
Temperature 300.0
Number of Scans 16
Receiver Gain 101
Relaxation Delay 1.0000
Pulse Width 14.8000
Frequency 400.15
Nucleus 1H
NO2
34
3.03
1.96
1.97
2.04
f1 (ppm)


135.75
129.11
128.70
127.59
76.42
33.60
Parameter Value
Title AAG-03044-D
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 9.0000
Frequency 150.97
Nucleus 13C
NO2
34
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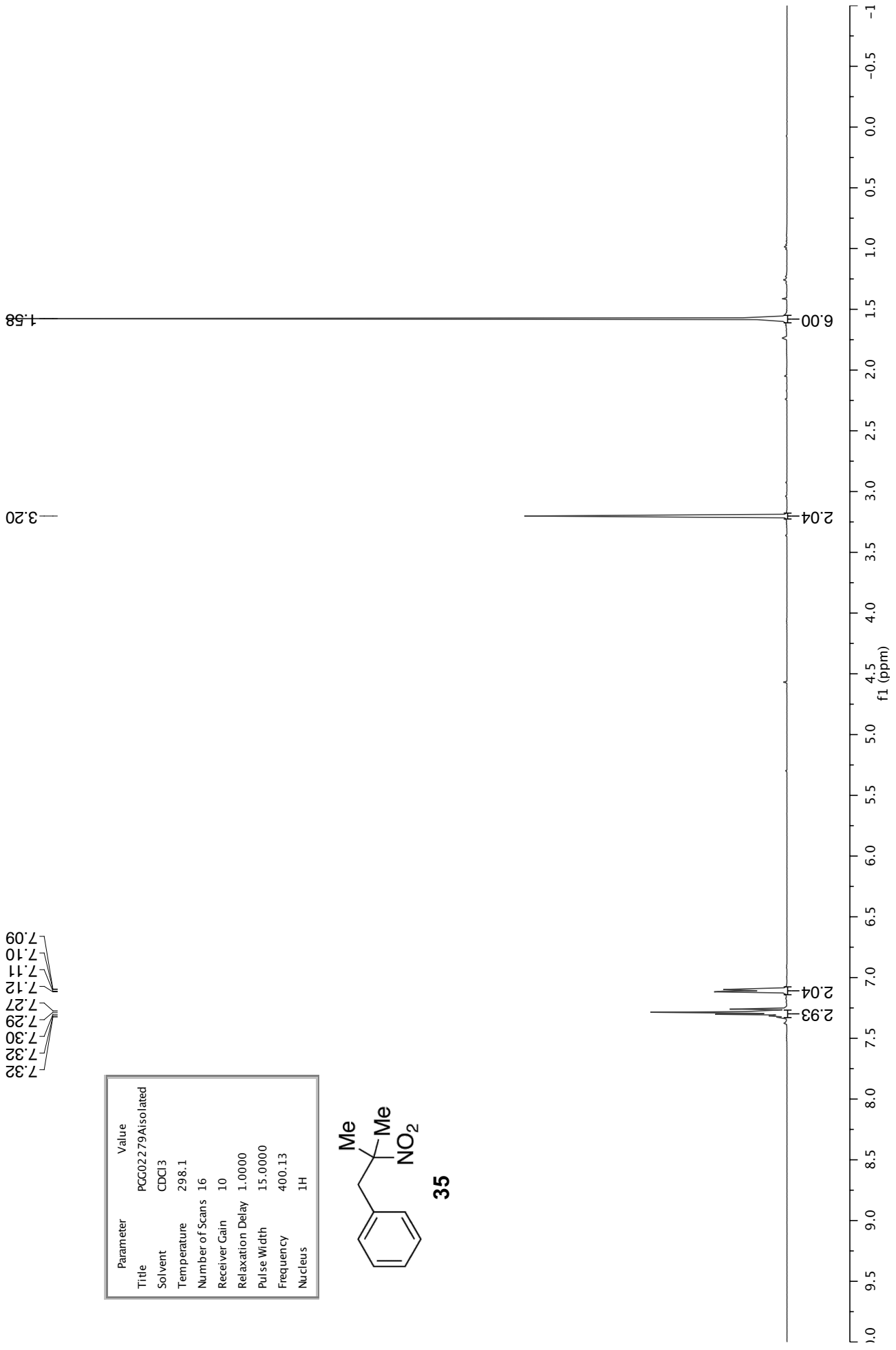
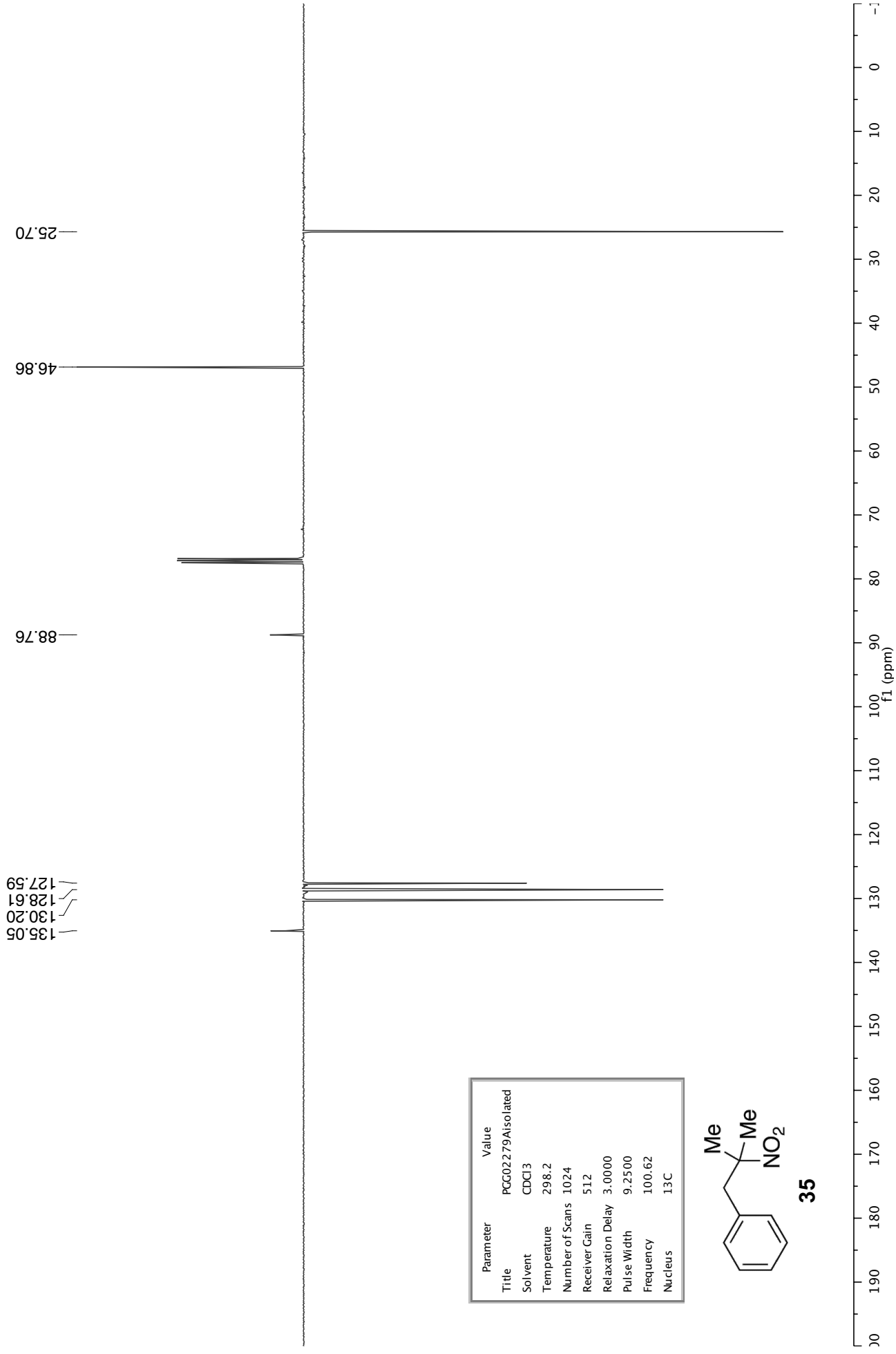
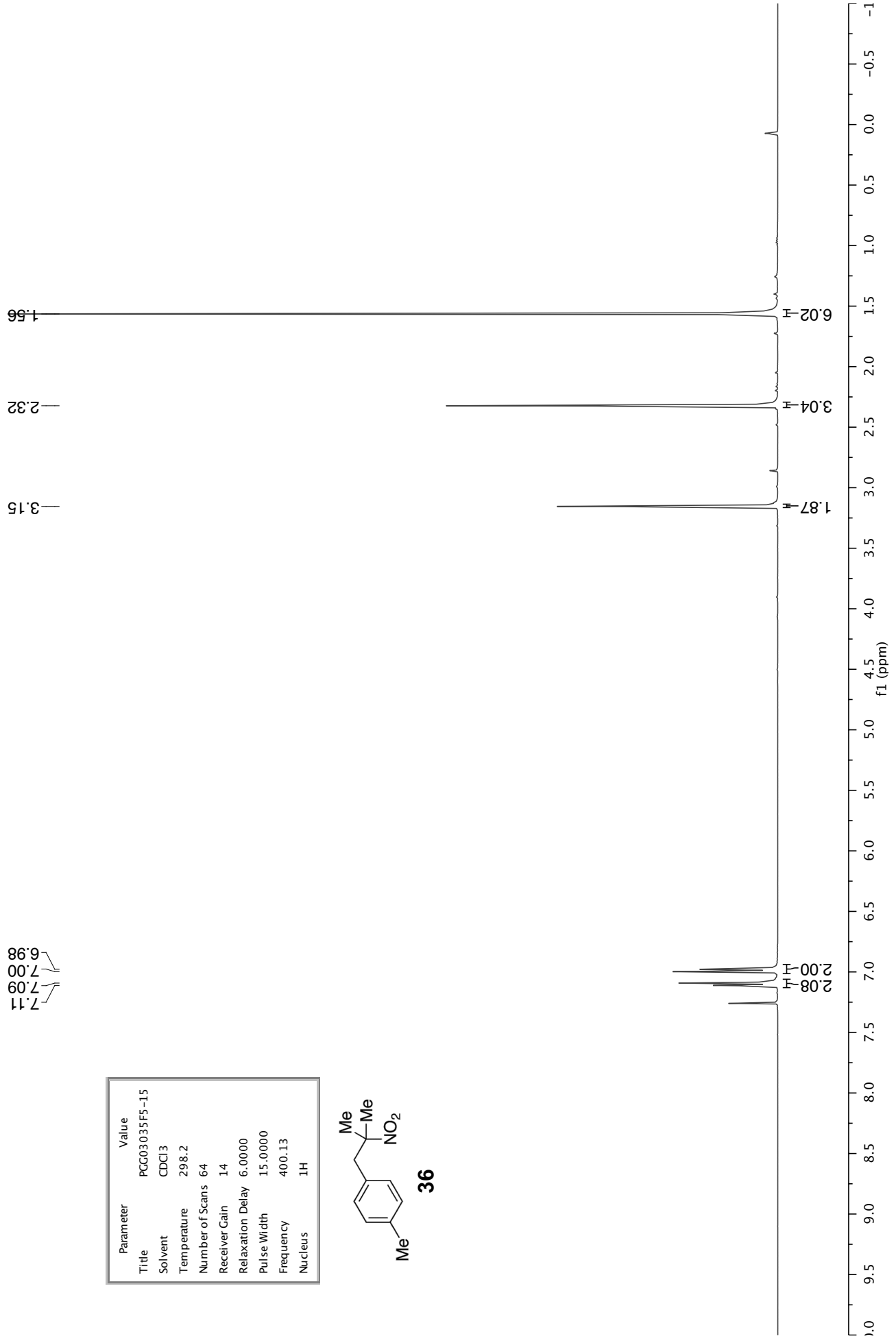
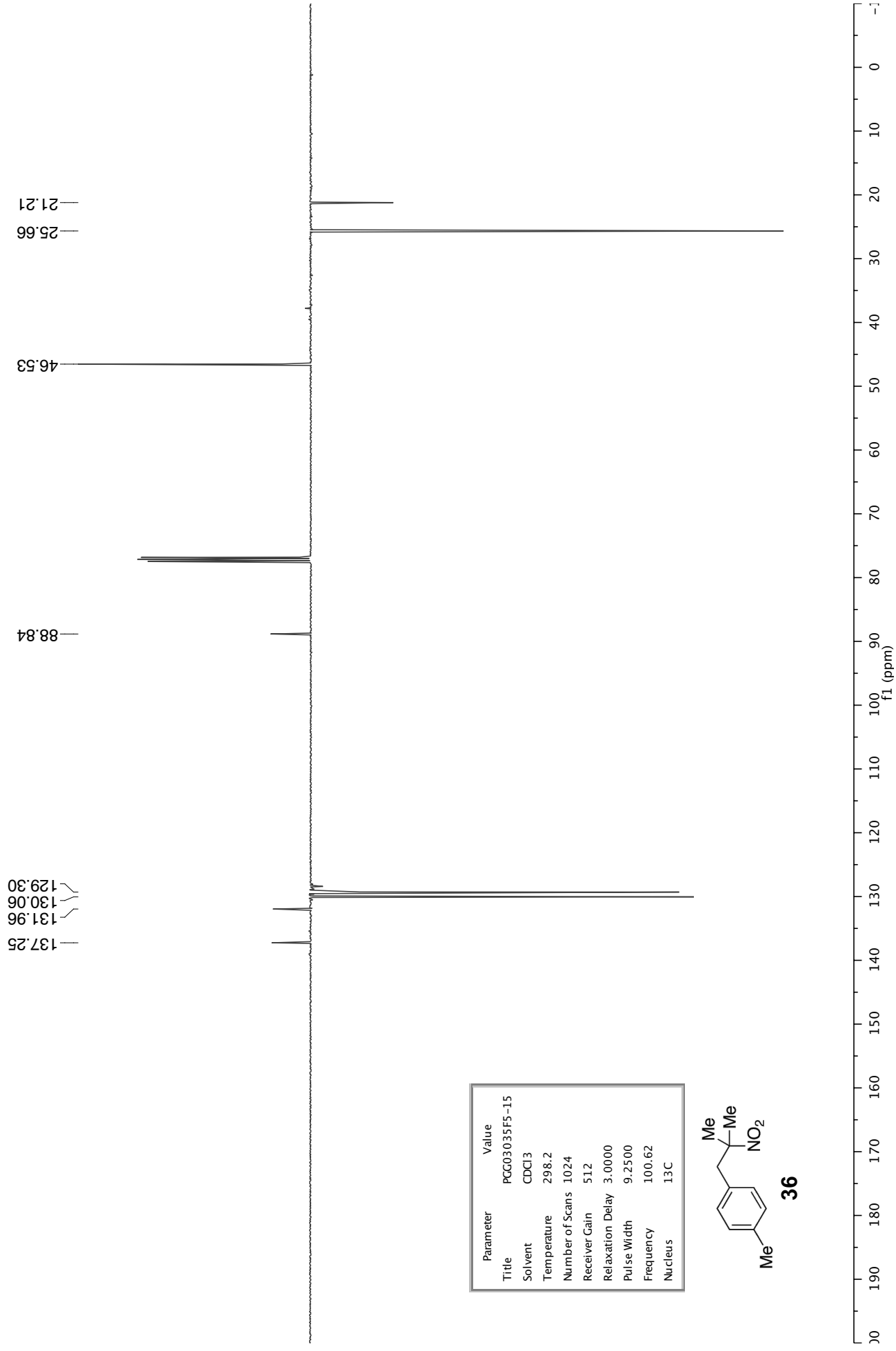
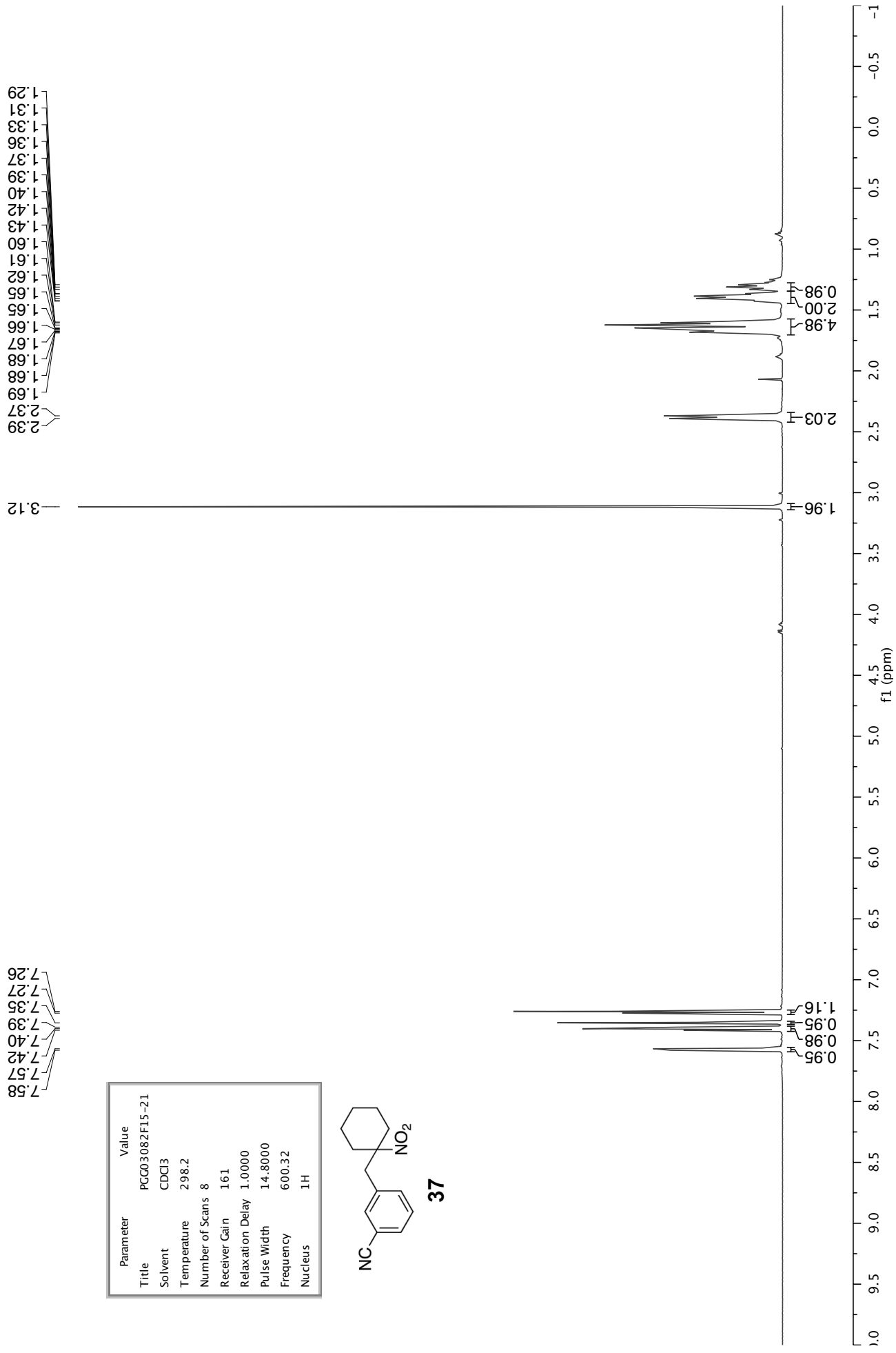
S71
f1 (ppm)

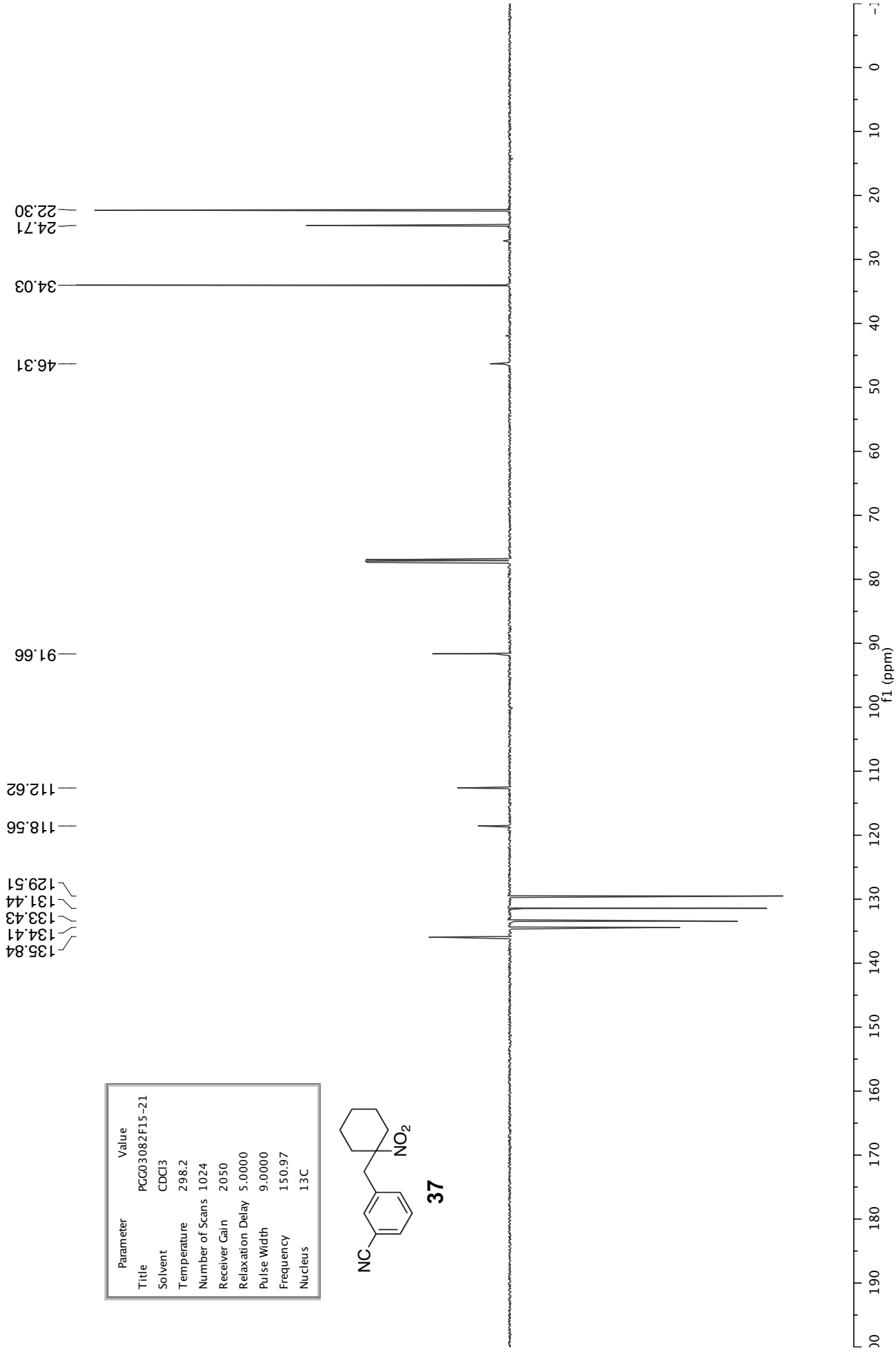

7.32
7.32
7.30
7.29
7.27
7.12
7.11
7.10
7.09
3.20
1.58
6.00
2.04
2.93
2.04
f1 (ppm)
Parameter Value
Title PGG02279Aisolated
Solvent CDCl3
Temperature 298.1
Number of Scans 16
Receiver Gain 10
Relaxation Delay 1.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
Me
Me
NO2
35

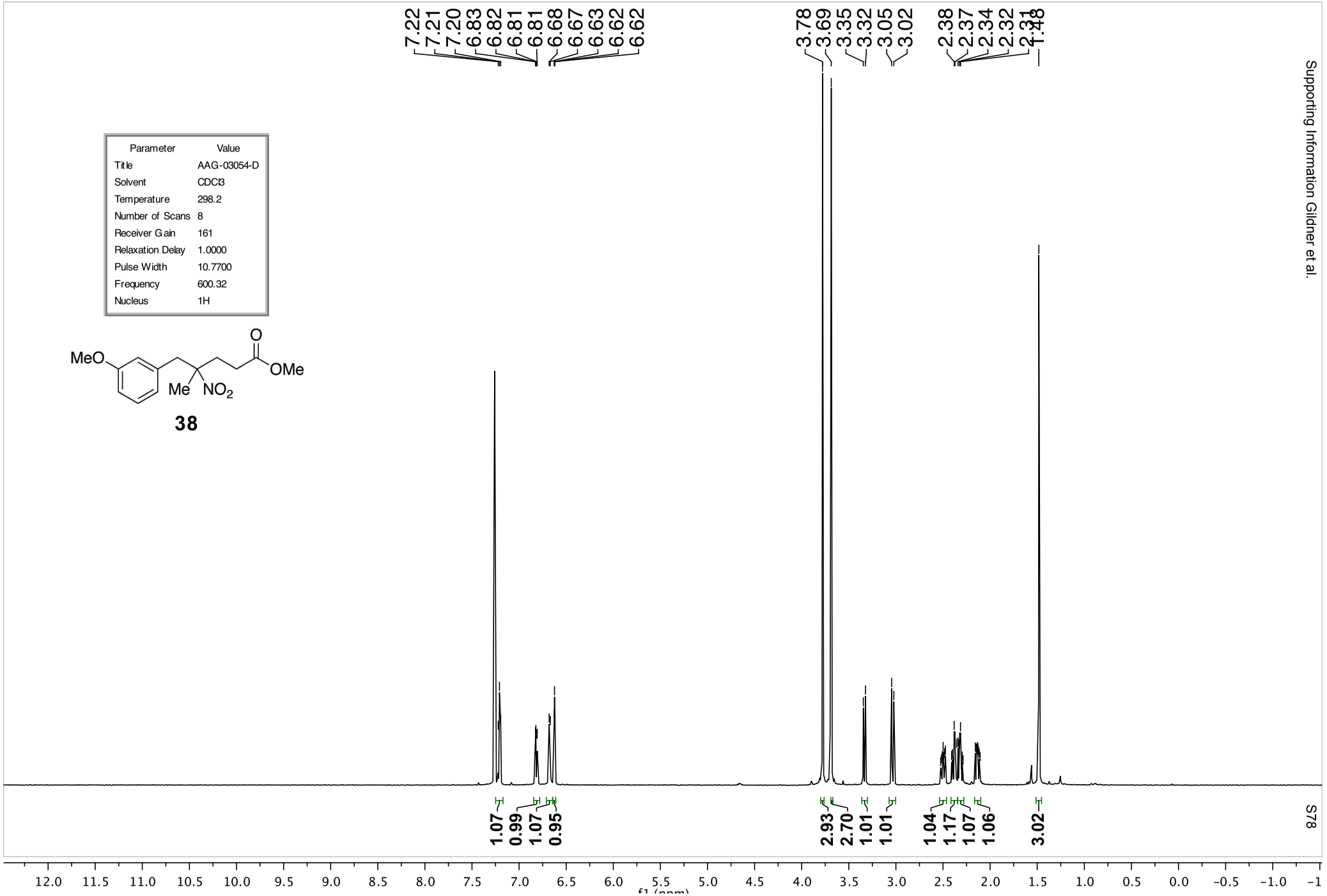

25.70
46.86
88.76
127.59
128.61
130.20
135.05
f1 (ppm)
Parameter Value
Title PGG02279Aisolated
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
Me
Me
NO2
35

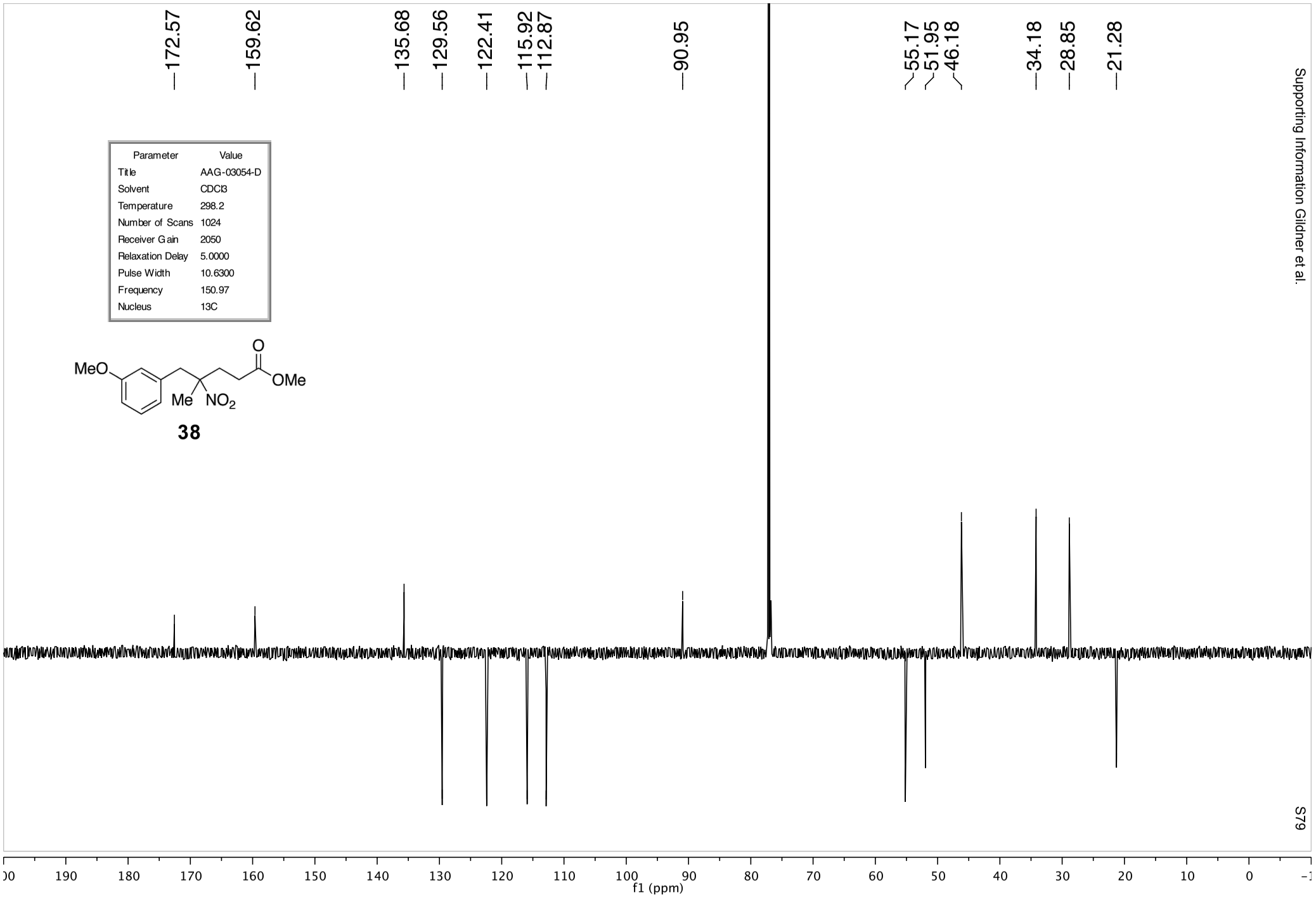

Parameter Value
Title PGG03035F5-15
Solvent CDCl3
Temperature 298.2
Number of Scans 64
Receiver Gain 14
Relaxation Delay 6.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
Me
Me
NO2
Me
36
7.11
7.09
7.00
6.98
3.15
2.32
1.56
2.08
2.00
1.87
3.04
6.02
f1 (ppm)

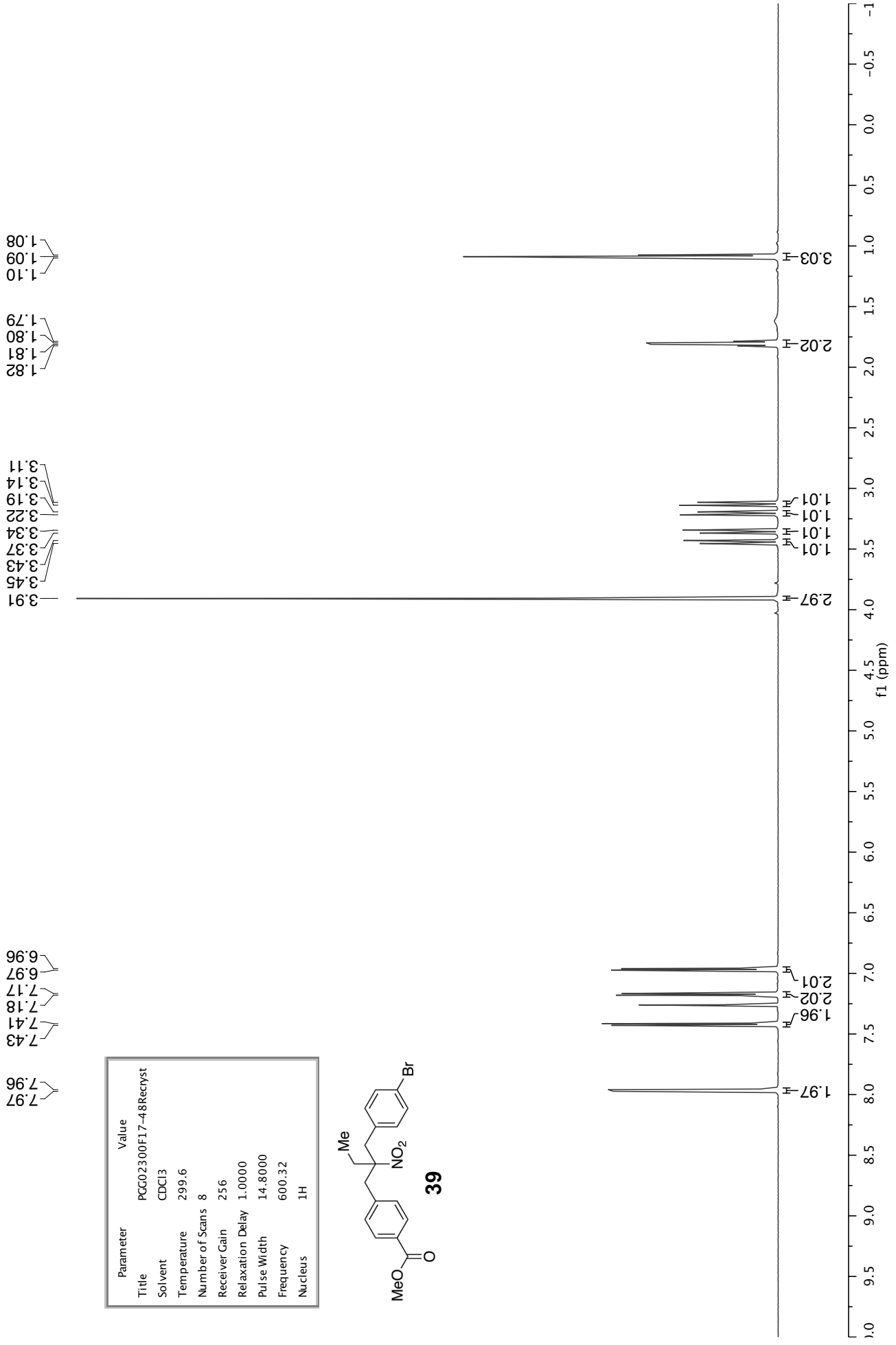

21.21
25.66
46.53
88.84
129.30
130.06
131.96
137.25
f1 (ppm)
Parameter Value
Title PGG03035F5-15
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
Me
Me
NO2
Me
36

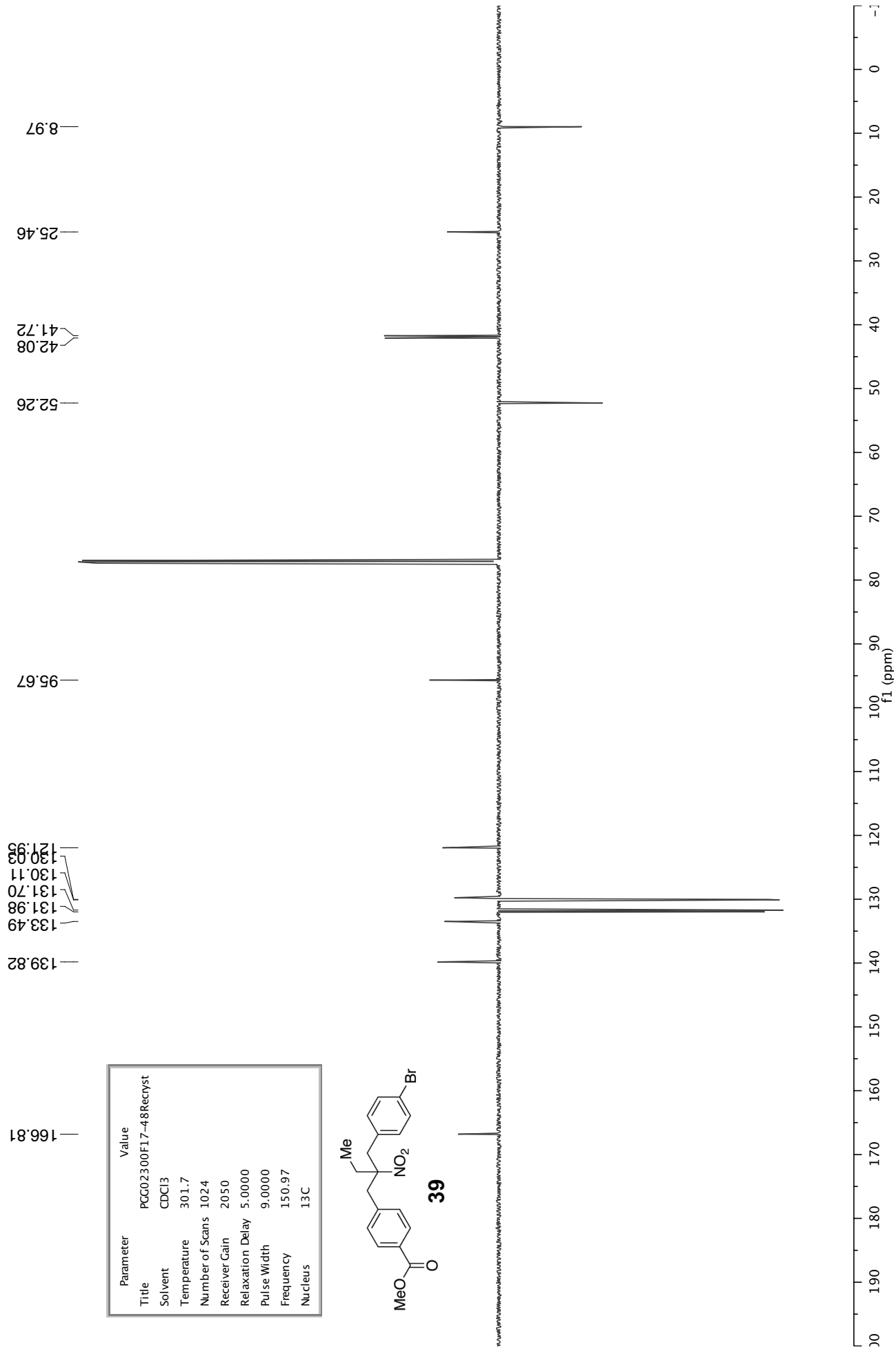

Parameter Value
Title PGG03082F15-21
Solvent CDCl3
Temperature 298.2
Number of Scans 8
Receiver Gain 161
Relaxation Delay 1.0000
Pulse Width 14.8000
Frequency 600.32
Nucleus 1H
NC
NO2
37
f1 (ppm)

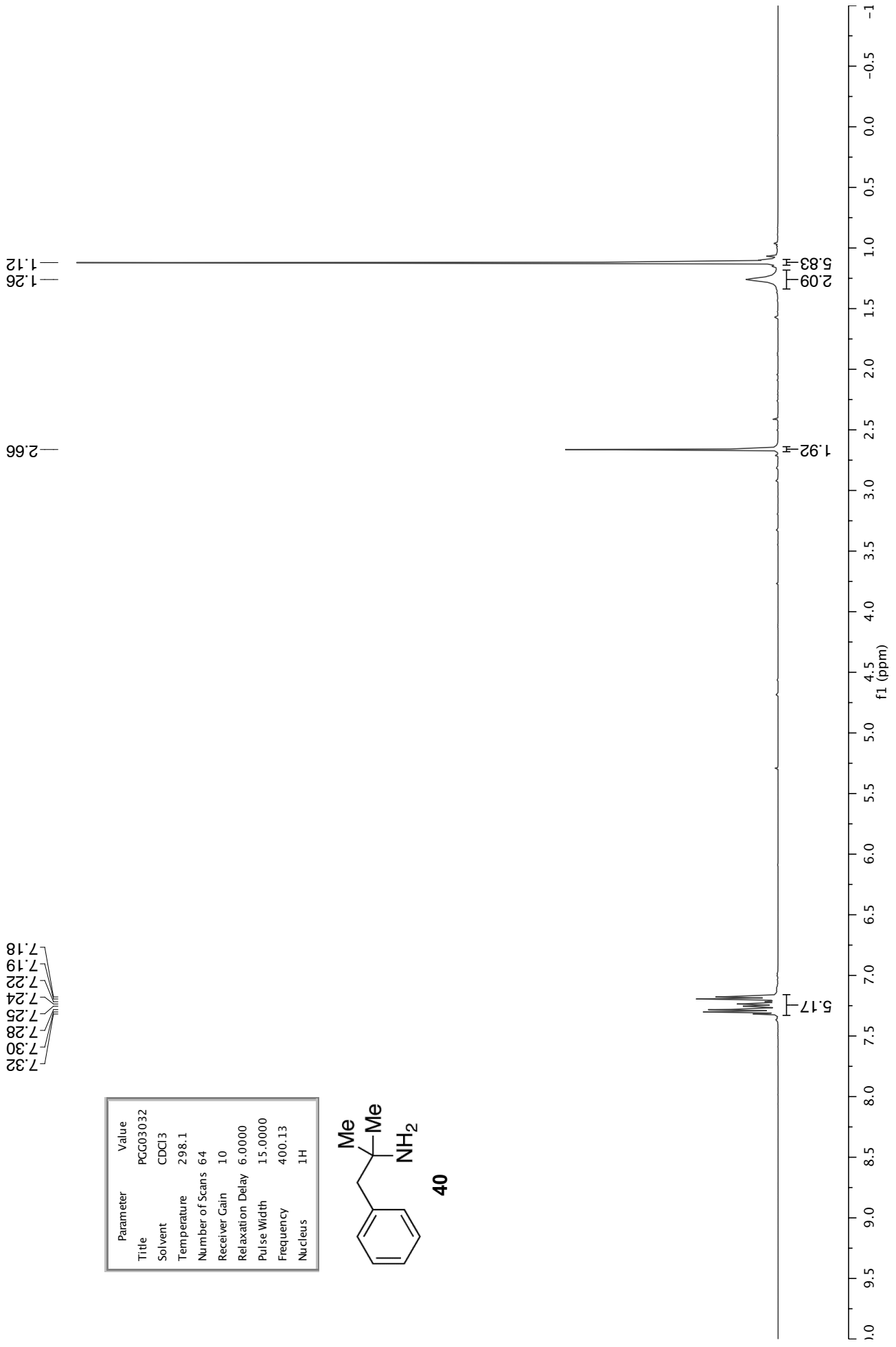

22.30
24.71
34.03
46.31
91.66
112.62
118.56
129.51
131.44
133.43
134.41
135.84
f1 (ppm)
Parameter Value
Title PGG03082F15-21
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 9.0000
Frequency 150.97
Nucleus 13C
NC
NO2
37

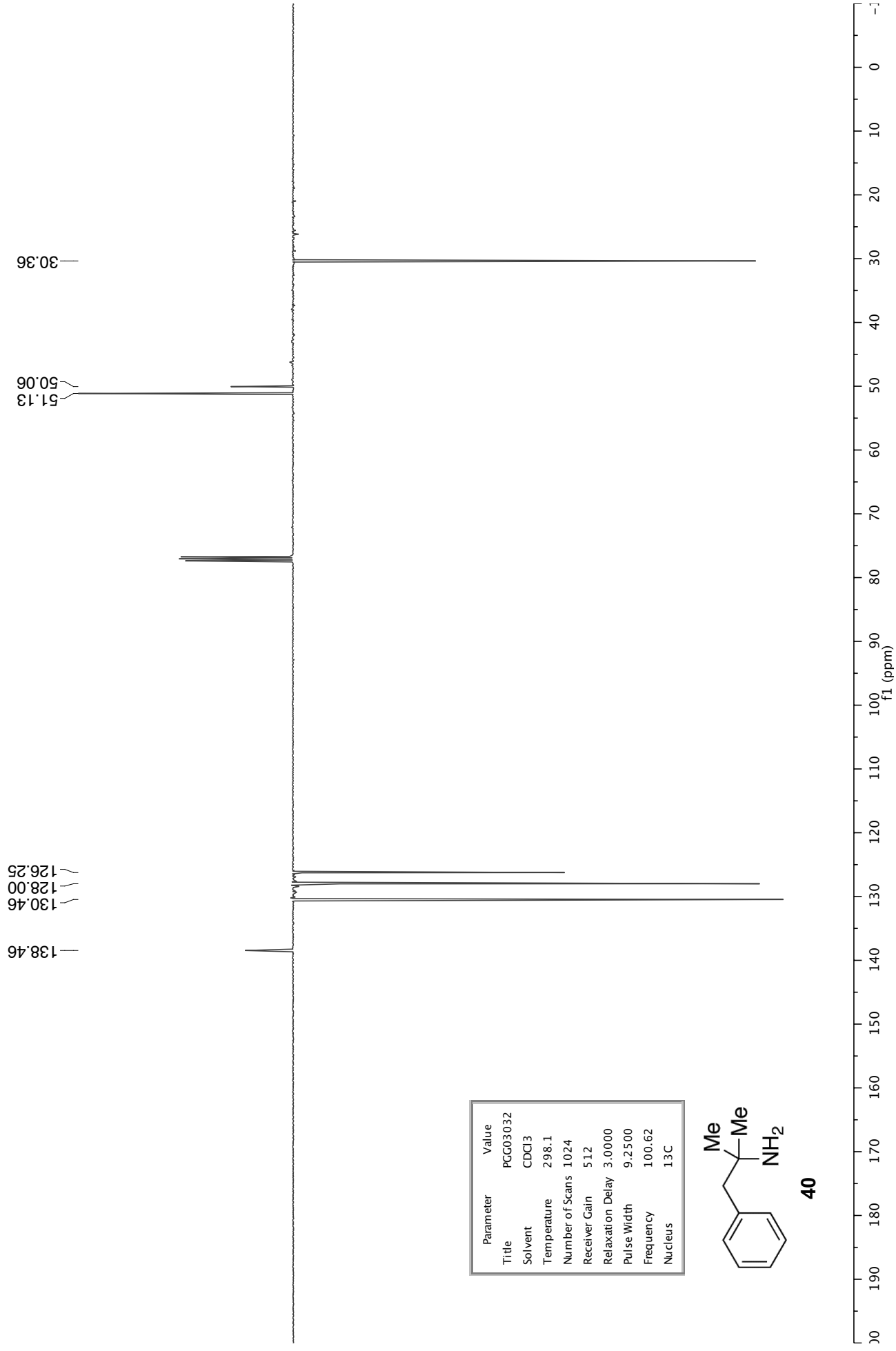

7.22
7.21
7.20
6.83
6.82
6.81
6.81
6.68
6.67
6.63
6.62
6.62
3.78
3.69
3.35
3.32
3.05
3.02
2.38
2.37
2.34
2.32
2.31
1.48
Parameter Value
Title AAG-03054-D
Solvent CDCl3
Temperature 298.2
Number of Scans 8
Receiver Gain 161
Relaxation Delay 1.0000
Pulse Width 10.7700
Frequency 600.32
Nucleus 1H
MeO
OMe
O
Me
NO2
38
1.07
0.99
1.07
0.95
2.93
2.70
1.01
1.01
1.04
1.17
1.07
1.06
3.02
12.0
11.5
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
-1.0
-1
f1 (ppm)


172.57
159.62
135.68
129.56
122.41
115.92
112.87
90.95
55.17
51.95
46.18
34.18
28.85
21.28
Parameter Value
Title AAG-03054-D
Solvent CDCl3
Temperature 298.2
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 10.6300
Frequency 150.97
Nucleus 13C
MeO
OMe
Me
NO2
O
38
f1 (ppm)


Parameter Value
Title PGG02300F17-48Recryst
Solvent CDCl3
Temperature 299.6
Number of Scans 8
Receiver Gain 256
Relaxation Delay 1.0000
Pulse Width 14.8000
Frequency 600.32
Nucleus 1H
Me
NO2
Br
MeO
O
39
f1 (ppm)


8.97
25.46
41.72
42.08
52.26
95.67
121.93
130.03
130.11
131.70
131.98
133.49
139.82
166.81
Parameter Value
Title PGG02300F17-48Recryst
Solvent CDCl3
Temperature 301.7
Number of Scans 1024
Receiver Gain 2050
Relaxation Delay 5.0000
Pulse Width 9.0000
Frequency 150.97
Nucleus 13C
Me
NO2
Br
MeO
O
39
f1 (ppm)


7.32
7.30
7.28
7.25
7.24
7.22
7.19
7.18
2.66
1.26
1.12
5.17
1.92
2.09
5.83
f1 (ppm)
Parameter Value
Title PGG03032
Solvent CDCl3
Temperature 298.1
Number of Scans 64
Receiver Gain 10
Relaxation Delay 6.0000
Pulse Width 15.0000
Frequency 400.13
Nucleus 1H
Me
Me
NH2
40


30.36
50.06
51.13
126.25
128.00
130.46
138.46
f1 (ppm)
Parameter Value
Title PGG03032
Solvent CDCl3
Temperature 298.1
Number of Scans 1024
Receiver Gain 512
Relaxation Delay 3.0000
Pulse Width 9.2500
Frequency 100.62
Nucleus 13C
Me
Me
NH2
40